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Part I

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INFLUENCE OF ROCK PHOSPHATES AND BASIC SLAGS ON THE  
PHOTOCHEMICAL OXIDATION OF SODIUM NITRITE

By

N. R. DHAR and R. N. TIWARI

*Sheila Dhar Institute of Soil Science, Allahabad University, Allahabad*

[ Received on 24th October, 1964 ]

ABSTRACT

We have studied the influence of Algerian rock phosphate, Trichinopoly rock phosphate, Kulti basic slag and Tata basic slag using  $ZnO$ ,  $TiO_2$  and  $SiO_2$  as photocatalysts on the photochemical oxidation of sodium nitrite and have noted that there is greater oxidation of nitrite in presence of slags and rock phosphates than without their presence. The order of oxidation of nitrite can be represented in the following decreasing order :—

T.B.S. > K.B.S. > T.R.P. > A.R.P.

Zinc oxide is the best photocatalyst amongst the photocatalysts used.

It is well known that plants mainly take up nitrogen in the form of nitrates from the fertilizers and soils, but all the nitrogen in the soil does not exist in the form of nitrates. It exists in various forms such as organic nitrogen, ammoniacal nitrogen and very little in the form of nitrites etc. Warington (1) showed that the nitrification is really the joint effect of the two organisms, one converts ammonium salts into nitrites but fails to change nitrites into nitrates even after the lapse of several years. The subsequent conversion of nitrites to nitrate is the work of another organism. P. F. and G. C. Frankland (2) isolated bacilloccoccus which produces nitric

acid from ammonium salts, Winogradsky (3) observed that the bacteria which transforms the nitrites to nitrates, have no action on ammonium salts.

Winogradsky (4) emphasized the ubiquitous distribution of the bacteria concerning with the nitrification; he found them in many soils, sea water, in drainage water etc. The agencies as described by Warington and Winogradsky for the process of nitrification are the living beings which can survive under suitable atmospheric conditions. The work of Roche, St. von Bazarwsky and G. G. A. Weber (5) showed that the most suitable temperature for bacterial nitrification is 25-27°C. But in the tropical countries like India, the soil temperature in the summer shoots upto (40-70°C) which renders the survival of these bacteria very difficult.

Hence, Prof. Dhar put forward the view that the process of nitrification is more photochemical than bacterial, specially in the soils of the tropical countries where the number of bacteria are small and are being mostly killed by the high temperature of the soil during summer.

Dhar, Tandon, Biswas and Bhattacharya (6) reported that dilute solutions of alkali nitrites are when exposed to sunlight in presence of photocatalysts like Zinc oxide, Titania, ferric oxide etc. are oxidised to nitrates.

In the present paper the authors have studied the influence of phosphate containing materials like Algerian rock phosphate, Trichinopoly rock phosphate, Kulti basic slag and Tata basic slag on the photochemical oxidation of sodium nitrite using Zinc oxide, Titania and Silica as photocatalyst.

#### *Experimental :—*

The photocatalysts  $ZnO$ ,  $SiO_2$  and  $TiO_2$  were washed with distilled water in order to remove all the impurities and was finally dried. Then 0.0985 gm of nitrogen in the form of sodium nitrite was mixed with 5.0 gms of photocatalyst and calculated amounts of Kulti and Tata basic slags and Algerian and Trichinophly rock phosphates were added to the systems. These mixtures were made uniform and were kept in the test tubes of equal dimensions. After that the experiments were performed under sterile and unsterile conditions, both being exposed to light under 100 watt electric bulb and in the dark.

After the exposure, the whole system was washed thoroughly with distilled water and in the filtrate, the nitrite unoxidised and nitrate formed were estimated. Total nitrogen was estimated by sulpho salicylic acid reduction method.

*N.B.:—*Total  $P_2O_5$  contents of these phosphate containing materials are Tata basic slag = 7.57% Kulti basic slag = 4.85% Algerian rock phosphate = 19.25% and Trichinopoly rock phosphate = 27.60%.

TABLE I

 $\text{NO}_2$  — Nitrogen (as  $\text{NaNO}_2$ ) = 0.0985 gm.

Total Nitrogen = 0.09859 gm.

Water = 5.0 cc

5.0 gms of  $\text{ZnO}$  as surface

(Under 100 watt Electric bulb)

Name of the phosphate added	Time for exposure in hours	Phosphate added as $\text{P}_2\text{O}_5$ in gm.	$\text{NO}_2 - \text{N}$ in gm	$\text{NO}_3 - \text{N}$ in gm	$\text{NaNO}_2$ oxidised in %
UNSTERILE CONDITIONS					
Algerian rock phosphate ...	35	0.138 0.414	0.0736 0.0592	0.02499 0.03939	22.27 39.89
Trichinopoly rock Phosphate	... „	0.138 0.414	0.0700 0.0565	0.02859 0.04209	28.93 42.63
Kulti basic slag	... „	0.138 0.414	0.0677 0.0549	0.03089 0.04369	31.24 44.26
Tata basic slag	... „	0.188 0.414	0.0652 0.0516	0.03339 0.04799	33.97 47.61
Without phosphate	... „	—	0.0786	0.01997	20.21
STERILE CONDITION					
Algerian rock phosphate ...	„	0.138 0.414	0.0872 0.0782	0.01132 0.02039	11.47 20.60
Trichinopoly rock Phosphate	... „	0.138 0.414	0.0853 0.0759	0.01329 0.02269	13.40 22.94
Kulti basic slag	... „	0.138 0.414	0.0828 0.0739	0.01579 0.02469	15.93 24.97
Tata basic slag	... „	0.138 0.414	0.0790 0.0713	0.01959 0.02729	19.79 27.61
Without phosphate	... „	—	0.0902	0.00839	8.42

$$\text{NO}_2 - \text{N}_2 \text{ (as NaNO}_2\text{)} = 0.0985 \text{ gm}$$

$$\text{Total Nitrogen} = 0.09859 \text{ gm.}$$

$$\text{Water} = 5.0 \text{ c.c.}$$

$$5.0 \text{ gm of ZnO as surface.}$$

(Under 100 watt Electric bulb)

Name of the phosphate added	Time for exposure in hours	Phosphates added as P <sub>2</sub> O <sub>5</sub> in gm	NO <sub>2</sub> -N in gm	NO <sub>3</sub> -N in gm	NaNO <sub>2</sub> oxidised in %
UNSTERILE CONDITION					
Algerian rock phosphate	300	0.138 0.414	0.0420 0.0300	0.05650 0.06854	49.74 63.95
Trichinology rock phosphate	,,	0.138 0.414	0.0401 0.0281	0.05842 0.07056	59.28 71.47
Kulti basic slag	,,	0.138 0.414	0.0380 0.0032	0.06050 0.09534	61.42 97.70
Tata basic slag	,,	0.138 0.414	0.0226 —	0.07596 0.09856	77.05 100.00
Without phosphate	,,	—	0.0450	0.04289	54.31
STERILE CONDITION					
Algerian rock phosphate	,,	0.138 0.414	0.0610 0.0494	0.03755 0.04915	38.09 49.84
Trichinopoly rock phosphate	,,	0.138 0.414	0.0570 0.0446	0.04155 0.05395	42.13 54.72
Kulti basic slag	,,	0.138 0.414	0.0529 0.0310	0.04565 0.06755	46.29 68.52
Tata basic slag	,,	0.138 0.414	0.0487 0.0250	0.04988 0.07258	50.55 74.61
Without phosphate	,,	—	4.0651	0.03345	33.90

TABLE 2

$\text{NO}_2$  = Nitrogen (as  $\text{NaNO}_2$ ) = 0.0985 gm.

Total - Nitrogen = 0.09859 gm.

Water = 5.0 c.c.

5.0 gm of  $\text{TiO}_2$  as surface.

(Under 100 watt Electric bulb)

Name of the phosphate added	Time for exposure in hours	Phosphate added as $\text{P}_2\text{O}_5$ in gm	$\text{NO}_2-\text{N}$ in gm	$\text{NO}_3-\text{N}$ in gm	$\text{NaNO}_2$ oxidised in %
UNSTERILE CONDITIONS					
Algerian rock phosphate	35	0.138 0.414	0.0745 0.0611	0.02409 0.03749	24.36 37.96
Trichinopoly rock phosphate	,,	0.138 0.414	0.0713 0.0582	0.02729 0.04039	27.61 40.91
Kulti basic slag	,,	0.138 0.414	0.0691 0.0582	0.02949 0.04229	22.84 42.84
Tata basic slag	,,	0.138 0.414	0.0669 0.0424	0.03169 0.05619	32.08 46.80
Without phosphate	,,	—	0.0801	0.01849	18.68
STERILE CONDITION					
Algerian rock phosphate	,,	0.138 0.414	0.887 0.0797	0.00989 0.01989	9.94 19.08
Trichinopoly rock phosphate	,,	0.138 0.414	0.0872 0.0779	0.01139 0.02069	11.47 20.91
Kulti basic slag	,,	0.138 0.414	0.0839 0.0760	0.01469 0.02259	14.82 22.86
Tata basic slag	,,	0.138 0.414	0.0800 0.0713	0.01859 0.02729	18.78 27.61
Without phosphate	,,	—	0.0910	0.00759	7.61

$\text{NO}_2$  — Nitrogen (as  $\text{NaNO}_2$ ) = 0.0985 gm

Total — Nitrogen = 0.09859 gm.

Water = 5.0 c.c.

5.0 gm of  $\text{TiO}_2$  as surface.

(Under 100 watts Electric bulb)

Name of the phosphate added	Time for exposure in hours	Phosphated added as $\text{P}_2\text{O}_5$ in gm	$\text{NO}_2-\text{N}_2$ in gm	$\text{NO}_3-\text{N}_2$ in gm	$\text{NaNO}_2$ oxidised in %
UNSTERILE CONDITION					
Algerian rock phosphate	300	0.138	0.0475	0.05102	51.77
		0.414	0.0350	0.05501	55.83
Trichinopoly rock phosphate	„	0.138	0.0435	0.05501	55.83
		0.414	0.0315	0.06704	68.02
Kulti basic slag	„	0.138	0.0409	0.05763	58.47
		0.414	0.0290	0.06955	70.56
Tata basic slag	„	0.138	0.0292	0.05936	73.55
		0.414	0.0010	0.09846	98.90
Without phosphate	„	—	0.0540	0.04645	45.07
STERILE CONDITION					
Algerian rock phosphate	„	0.138	0.0690	0.02957	29.94
		0.414	0.0540	0.04458	45.17
Trichinopoly rock phosphate	„	0.138	0.0621	0.03646	39.95
		0.414	0.0483	0.05027	49.94
Kulti basic slag	„	0.138	0.0591	0.03947	40.00
		0.414	0.0464	0.05218	52.89
Tata basic slag	„	0.138	0.0514	0.04718	47.81
		0.414	0.0301	0.06849	69.54
Without phosphate	„	—	0.0751	0.02338	23.75

TABLE 3

NO<sub>2</sub> — Nitrogen (as NaNO<sub>2</sub>) = 0.0985.

Total — Nitrogen = 0.09859 gm.

Water = 50 c.c.

5.0 gms of Silica as surface.

(Under 100 watt Electric bulb)

Name of the phosphate added	Time for exposure in hours	Phosphate added as P <sub>2</sub> O <sub>5</sub> in gm	NO <sub>2</sub> -N in gm	NO <sub>3</sub> -N in gm	NaNO <sub>2</sub> oxidised in %
UNSTERILE CONDITION					
Algerian rock phosphate	35.0	0.138 0.414	0.0779 0.0632	0.02069 0.03039	20.91 30.76
Trichinopoly rock phosphate	„	0.138 0.414	0.0731 0.0612	0.02549 0.03739	25.78 37.86
Kulti basic slag	„	0.138 0.414	0.0703 0.0881	0.02829 0.04049	88.62 41.01
Tata basic slag	„	0.138 0.414	0.0672 0.0553	0.03139 0.04329	31.77 43.85
Without phosphate	„	—	0.0843	0.01429	14.41
STERILE CONDITION					
Algerian rock phosphate	„	0.138 0.414	0.0916 0.0832	0.00699 0.1539	7.10 15.53
Trichinopoly rock phosphate	„	0.138 0.414	0.0894 0.0788	0.00919 0.01979	9.23 20.00
Kulti basic slag	„	0.138 0.414	0.0864 0.0787	0.01219 0.01989	12.28 20.10
Tata basic slag	„	0.138 0.414	0.0818 0.0732	0.01679 0.02539	16.95 25.68
Without phosphate	„	—	0.0959	0.00309	2.62

$\text{NO}_2$  - Nitrogen (as  $\text{NaNO}_2$ ) = 0.0985 gm.

Total - Nitrogen = 0.09859 gm.

Water = 5.0 c.c.

5.0 gms of Silica as surface.

(Under 100 watts Electric bulb)

Name of the phosphate added	Time for exposure in gms	Phosphate added as $\text{P}_2\text{O}_5$ in gm	$\text{NO}_2 - \text{N}_2$ in gm	$\text{NO}_3 - \text{N}_2$ in gm	$\text{NaNO}_2$ oxidised in %
UNSTERILE CONDITION					
Algerian rock phosphate	300.0	0.138 0.414	0.0513 0.0373	0.04724 0.06128	47.91 62.13
Trichinopoly rock phosphate	„	0.138 0.414	0.0483 0.0350	0.05026 0.06359	50.97 64.46
Kulti basic slag	„	0.138 0.414	0.0449 0.0319	0.05368 0.06669	54.41 67.61
Tata basic slag	„	0.138 0.414	0.0310 0.0120	0.06759 0.07659	68.52 87.81
Without phosphate	„	—	0.0591	0.03942	40.41
STERILE CONDITION					
Algerian rock phosphate	„	0.138 0.414	0.0720 0.0560	0.02659 0.04259	26.90 43.14
Trichinopoly rock phosphate	„	0.138 0.414	0.0670 0.0493	0.03159 0.04929	31.97 45.98
Kulti basic slag	„	0.138 0.414	0.0640 0.0493	0.03459 0.04929	35.02 45.98
Tata basic slag	„	0.138 0.414	0.0490 0.0340	0.04959 0.06459	50.25 65.48
Without phosphate	„	—	0.0815	0.01703	17.25

Table one shows the influence of Algerian rock phosphates, Trichinopoly rock phosphate. Kulti basic slag and Tata basic slag on the photochemical oxidation of sodium nitrite using Zinc oxide as surface both under unsterile and sterile condition. With 0.0935 gm of nitrogen as sodium nitrite and 5.0 gms of surface in presence of 0.138 gm of  $P_2O_5$  as Algerian rock phosphates the oxidation of sodium nitrite is 25.27% and when the amount of phosphate is increased to 0.414 gm the oxidation of nitrite is 39.89 % after 35 hours. In the same way, the oxidation of sodium nitrite was studied in presence of Trichinopoly rock phosphate, Kulti basic slag and Tata basic slag, the maximum oxidation of nitrite in presence of 0.414 gm  $P_2O_5$  are 42.63, 44.26 and 45.61 % respectively after 35 hours, and without phosphates the oxidation of nitrite is 20.21 % only. Thus, by the addition of these phosphates, the oxidation of sodium nitrite increases and it also increases with the addition of increased amount of these phosphates.

When the time of exposure is increased to 300 hours, the oxidation of sodium nitrite still increases. A remarkable fact has been observed that in 300 hours exposure in presence of 0.414 gm of Tata basic slag as  $P_2O_5$  the whole of the sodium nitrite is oxidised. Without phosphate the oxidation of sodium nitrite is 54.31 %.

Similar experiments have been performed under sterile condition and it has been observed that 0.0985 gm of Nitrogen as sodium nitrite, 5.0 gms of  $ZnO$  and 5.0 ml of distilled water the oxidation of sodium nitrite in presence of 0.138 gm of Algerian rock phosphate is 11.47 % and when the amount of phosphate is increased to 0.414 gm, the oxidation of sodium nitrite becomes 20.61 %. In the same way, the maximum oxidation of sodium nitrite in presence of 0.414 gm of Trichinopoly rock phosphate, Kulti basic slag and Tata basic slag are 22.94, 24.97 and 27.61 % respectively after 35 hours, without phosphate the oxidation of nitrite is 8.42 %. Here also when the time of exposure is increased to 300 hours under sterile condition, it has been observed that with the increase of time, the oxidation of sodium nitrite is increased.

This it is clear from the above experiments that the oxidation of sodium nitrite is greater in unsterile condition than that in the sterile one. It is beyond doubt that the process of nitrification is not wholly a bacterial one, but can take place without bacteria.

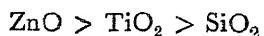
Similar experiments have been carried in dark also, both under sterile and unsterile conditions, and it has been observed that there is no oxidation of sodium nitrite in the dark.

In the same way, the experiments were carried out with 0.0985 gm of nitrogen as sodium nitrite, 5.0 gm of surface materials as Titania and Silica and 5.0 c.c. distilled water, under sterile and unsterile conditions, both in light and dark vide tables 2 and 3. The amounts of phosphate added as Algerian rock phosphate. Trichinopoly rock phosphate, Kulti basic slag and Tata basic slag is also maintained same as in Table 1. In every case, it has been observed that the oxidation of nitrite is always greater in unsterile sets than the sterile one. Secondly the oxidation of sodium nitrite is greater in the phosphated sets than the unphosphated sets. Thirdly, there is no oxidation of sodium nitrite in absence of surface and light. Dhar and Tandon (8) have also reported that there is no oxidation of sodium nitrite in the dark and in absence of photocatalysts. The results of Suryanaraya (7) also showed that there is no oxidation of sodium nitrite in the dark. The influence of

Tata basic slag, Kulti basic slag, Trichinopoly rock phosphate, and Algerian rock phosphate on the photo-chemical oxidation of sodium nitrite using  $ZnO$ ,  $TiO_2$  and  $SiO_2$  as surface are in the following decreasing order :—

Tata basic slag > Kulti basic slag > Trichinopoly rock phosphate > Algerian rock phosphate.

It has been observed from the above experiments that Zinc oxide is the best photocatalyst amongst the various photocatalysts. Dhar and Tondon (8) Systematically studied the conditions under which the dilute solutions of sodium nitrite undergo photochemical oxidation to nitrate when the system is exposed to sunlight, and they observed that Zinc oxide is the best photocatalyst, when they used  $TiO_2$ ,  $Fe_2O_3$  and  $ZnO$  as photocatalyst which is confirmed by these resuls also. The efficacy of the different photocatalysts used may be represented in the following decreasing order :—



The results obtained in this investigation has wide application in the field of Agriculture as these phosphate containing materialy like basic slags and rock phosphates are used as commercial phosphatic fertilizer in the field and it has been observed that by the addition of these phosphates the crop yield is considerably increased and in addition to the phosphate they contain, they also increase the available nitrogen of the soil.

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# COMPOUNDS OF ZIRCONIUM TETRABROMIDE WITH PHENOLS

By

SARJU PRASAD. (MISS) K. SHYAMALA DEVI and (MISS) MOMOTA BISWAS

*Chemical Laboratories, Banaras Hindu University, Varanasi-5*

[ Received on 15th September, 1964 ]

## ABSTRACT

Compounds of zirconium tetrabromide with some phenols have been prepared, their properties studied and structures discussed. With excess of phenol only substitution products are formed but with an excess of the zirconium tetrabromide aminophenols yield substitution-cum-coordination compounds.

A survey of the literature shows that no work has been carried out to study the formation of compounds of zirconium with phenols except that carried out by Jantsch<sup>1</sup> who studied the interaction of  $ZrCl_4$  with phenol and obtained the triphenolate  $Zr(OC_6H_5)_3Cl$  and the tetraphenolate  $Zr(OC_6H_5)_4$ . The present investigation was therefore undertaken with a view to studying the compounds of  $ZrBr_4$  with phenols in non-aqueous medium.

$ZrBr_4$  was prepared by passing dry bromine vapour over an intimate mixture of  $ZrO_2$  and carbon at red heat. This was extracted with anhydrous ethyl acetate and analysed for purity.

## EXPERIMENTAL

Ethyl acetate solution of  $ZrBr_4$  and an excess of phenol in ethyl acetate were mixed in a small flask the exit of which was connected with a number of drying tubes containing fused  $CaCl_2$  and  $P_2O_5$  and heated on a water bath till ethyl acetate was completely evaporated off. The flask was then heated in an electrically heated sandbath at a temperature about  $10^{\circ}C$  higher than the M.P.S. of the respective phenols till the evolution of HBr ceased. When the reaction was completed the product was taken out, washed with anhydrous ether, ethyl acetate or benzene till free from the reactants, all the operations being carried out in a dry atmosphere. It was dried in a vacuum desiccator and analysed.

In the case of amino phenols another set of experiments was carried out in which  $ZrBr_4$  was in excess.

### Analytical :

Zirconium was estimated as  $ZrO_2$ , bromine as silver bromide, in cases where it was present and the organic matter found by difference.

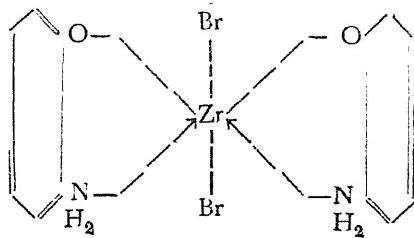
No.	Phenols	Compound form	Zirconium		Bromine	
			Found %	Calcd. %	Found %	Calcd. %
1.	$\alpha$ -Naphthol	Zr(C <sub>10</sub> H <sub>7</sub> O) <sub>4</sub> (alpha)	14.05	13.76	—	—
2.	$\beta$ -Naphthol	Zr(C <sub>10</sub> H <sub>7</sub> O) <sub>4</sub> (beta)	13.45	13.96	—	—
3.	$\alpha$ -Cresol	Zr(CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> O) <sub>4</sub> (ortho)	17.56	17.57	—	—
4.	p-Cresol	Zr(CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> O) <sub>4</sub> (para)	17.77	17.57	—	—
5.	Eugenol	Zr[(CH <sub>2</sub> .CH.CH <sub>2</sub> ).C <sub>6</sub> H <sub>3</sub> .(OCH <sub>3</sub> )O] <sub>4</sub>	11.98	12.27	—	—
6.	Phloroglucinol	Zr <sub>3</sub> (C <sub>6</sub> H <sub>3</sub> O <sub>3</sub> ) <sub>4</sub>	35.17	35.69	—	—
7.	Pyrocatechol	Zr(C <sub>6</sub> N <sub>4</sub> O <sub>2</sub> ) <sub>2</sub>	29.48	29.64	—	—
8.	Orcinol	Zr(CH <sub>3</sub> .C <sub>6</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	27.145	27.33	—	—
12	Hydroquinone	Zr(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub>	30.16	29.3?	—	—
10.	Pyrogallol	Zr <sub>3</sub> (C <sub>6</sub> H <sub>3</sub> O <sub>3</sub> ) <sub>4</sub>	35.36	35.69	—	—
11.	$\alpha$ -Nitro phenol	Zr(NC <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> O) <sub>4</sub>	14.11	14.19	—	—
12.	m-Nitro phenol	do	14.82	14.19	—	—
13.	2,4-dinitro phenol	Zr[(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O] <sub>4</sub>	11.56	11.09	—	—
14.	$\alpha$ -Amino phenol	Zr(NH <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> O) <sub>4</sub>	17.32	17.44	—	—
15.	m-Amino phenol	do	17.63	17.44	—	—
16.	p-Amino phenol	do	17.84	17.44	—	—
		With ZrBr <sub>4</sub> in excess				
17.	$\alpha$ -Amino phenol	Zr (NH <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Br <sub>2</sub>	19.15	19.54	33.95	34.22
18.	m-Amino phenol	do	19.59	19.54	34.48	34.22
19.	p-Amino phenol	do	19.17	19.54	34.02	34.22

*General properties of the compound :*

All the compounds were dark coloured, insoluble in water and common organic solvents. They were not acted up-on by dilute acids and alkalies. When heated with concentrated mineral acids they decomposed. They did not melt but decomposed at higher temperatures.

DISCUSSION

An examination of the results shows that one molecule of  $ZrBr_4$  reacts with four molecules of a monohydroxy, two of a dihydroxy phenol irrespective of the nitro groups present, and 3 molecules of it react with 4 molecules of a trihydroxy phenol, bromine being completely displaced in all the cases. When  $ZrBr_4$  is taken in excess substitution-cum-coordination result and chelated compounds as shown below are formed.



Thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

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# COMPOUNDS OF ZIRCONIUM TETRAHALIDES WITH ORGANIC ACIDS

By

SARJU PRASAD, (MISS) K. SHYAMALA DEVI and (MISS) KANTA SAHNEY

Chemical Laboratories, Banaras Hindu University, Varanasi-5

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## ABSTRACT

Compounds of zirconium tetrahalides with some organic acids have been prepared, their properties studied and structures discussed. With an excess of the acid only substitution products are formed but with an excess of the zirconium halide amino-acids yield substitution-cum-coordination compounds.

Though a number of zirconium salts with organic acids which are generally basic have been prepared in aqueous medium, the preparation of normal salts of zirconium with organic acids has not been studied systematically.

Jantsch<sup>1</sup> studied the interaction of  $ZrCl_4$  with benzoic acid in boiling benzene and obtained the compound  $Zr(C_6H_5COO)_4$ . With mandelic acid ester and methyl salicylate he obtained the addition products at  $-10^\circ$  and disubstitution products at higher temperatures; with the latter he obtained a trisubstitution products also at higher temperatures. Morgan and Bowen<sup>2</sup> obtained zirconium tris benzoyl methane chloride by the interaction of  $ZrCl_4$  with benzoyl methane in chloroform and also in benzene. He prepared it also by the interaction of  $ZrCl_4$  with copper di-benzoyl chloride. Rosenheim and Hertzman<sup>3</sup> studied the interaction of  $ZrCl_4$  with benzoic acid in ether at its boiling temperature and obtained the compound  $ZrCl_2(COOCH_3)_2$ . They however found that all the chlorine atoms were replaced when  $ZrCl_4$  was treated with formic, acetic or propionic acid yielding the normal salt in each case. On refluxing  $ZrCl_4$  with ethyl benzoate they obtained the addition compound  $ZrCl_4(C_6H_5COOC_2H_5)_2$ .

By heating  $ZrCl_4$  with excess of  $Ph.CH_2COOH$  Jaura, Banga and Kaushik obtained  $ZrCl_2.Pa_2$  (decompose at  $170^\circ C$ ), where Pa stands for ( $Ph.CH_2COO$ ), at  $110^\circ$  and  $ZrPa_4$  (m.p.  $122^\circ$ ) at  $135^\circ C$ . On heating stoichiometric amounts of  $ZrCl_4$  and  $PaH$  at  $120^\circ C$ , they obtained  $ZrCl_3(Pa_3)$  (m.p.  $133^\circ - 35^\circ C$ ).

The present investigation was therefore undertaken with a view to studying the preparation of normal salts of zirconium with organic acids.

## EXPERIMENTAL

The chemicals used were of B.D.H. or E. Mercks' extra pure quality.  $ZrX_4^*$  was prepared as described earlier (loc. cit.) by passing the respective halogen over a mixture of  $ZrO_2$  and sugar charcoal at red heat. It was extracted with dry ethyl acetate and analysed for purity.

An excess of ethyl acetate solution of the respective organic acid was added to the zirconium tetrahalide solution, the solvent removed by heating on a water bath. Finally the mixtures were heated on a sand bath kept at  $10^\circ C$  above the M.P. of the respective acid till the evolution of hydrogen halides ceased, care being taken

\*  $ZrCl_4$  was used for expts. 1-13 and  $ZrBr_4$  for 14 - 20.

No. of expts.	Organic substance	Compound formed	Colour	Zirconium			Bromine
				Found %	Calcd. %	Found %	Calcd. %
1.	Lauric acid	Zr(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COO) <sub>4</sub>	Brown	10.69	9.83	—	—
2.	Myristic acid	Zr(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COO) <sub>4</sub>	Blackish brown	8.79	9.221	—	—
3.	Palmitic acid	Zr(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COO) <sub>4</sub>	Ash	9.752	8.212	—	—
4.	Stearic acid	Zr(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COO) <sub>4</sub>	Ash	7.418	7.459	—	—
5.	Cinnamic acid	Zr(C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> COO) <sub>4</sub>	White (dirty)	14.15	13.43	—	—
6.	Benzoic acid	Zr(C <sub>6</sub> H <sub>5</sub> COO) <sub>4</sub>	Grey	15.65	15.85	—	—
7.	Phthalic acid	Zr(C <sub>6</sub> H <sub>4</sub> (COO) <sub>2</sub> ) <sub>2</sub>	Black	27.98	21.86	—	—
8.	Succinic acid	Zr(CH <sub>2</sub> ) <sub>2</sub> (COO) <sub>2</sub> <sub>a</sub>	White	28.22	—	—	—
9.	Adipic acid	Zr(CH <sub>2</sub> ) <sub>4</sub> (COO) <sub>2</sub> <sub>a</sub>	Black	23.69	24.06	—	—
10.	Salicylic acid	Zr [C <sub>6</sub> H <sub>4</sub> —   O—COO] <sub>2</sub>	Dark grey	24.53	24.44	—	—
11.	Malic acid	Zr[CH <sub>2</sub> CH(OH)(COO) <sub>2</sub> ] <sub>2</sub>	Ash	26.53	25.68	—	—
12.	Citric acid	Zr <sub>3</sub> [C(OH).COO—   {CH <sub>2</sub> .COO} <sub>4</sub> ] <sub>4</sub>	Dark grey	24.93	26.60	—	—
13.	Camphoric acid	Zr [C <sub>8</sub> H <sub>14</sub> —   COO] <sub>2</sub>	Black	15.75	13.79	—	—
14.	<i>o</i> -Nitrobenzoic acid	Zr(NO <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> COO) <sub>4</sub>	Black	12.30	12.08	—	—
15.	<i>m</i> -Nitrobenzoic acid	"	Black	12.58	12.08	—	—
16.	<i>p</i> -Nitrobenzoic acid	"	Black	12.15	12.08	—	—
17.	<i>o</i> -Aminobenzoic acid	Zr(NH <sub>2</sub> C <sub>6</sub> N <sub>4</sub> COO) <sub>4</sub>	Black	13.5 <sup>a</sup>	14.36	—	—
18.	<i>p</i> -Aminobenzoic acid	"	Black	13.29	14.36	—	—
			With ZrBr <sub>4</sub> in excess				
19.	<i>o</i> -Aminobenzoic acid	Zr(NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> Br <sub>2</sub>	Black	17.34	17.44	30.31	30.56
20.	<i>p</i> -Aminobenzoic acid	"	Black	17.21	17.44	30.32	30.56

that the exit tube was connected to a series of drying tubes containing fused  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$ . Another set of experiments was carried out in which  $\text{ZrX}_4$  was in excess. The reaction products were extracted with ethyl acetate, filtered the residue washed free of the reactants, dried in a vacuum desiccator and analyzed.

*Analytical :*

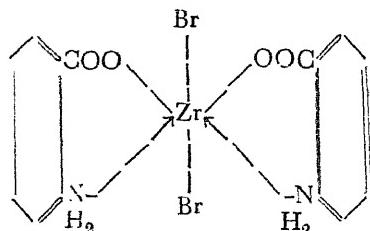
Zirconium was estimated as  $\text{ZrO}_2$  and halogen as silver halide by Piria and Schiffs' method.

*General properties :*

All the compounds were coloured, insoluble in organic solvents like benzene and ether. When heated they decomposed over  $200^\circ\text{C}$  without melting.

### DISCUSSION

An examination of the results shows that when an excess of acid is used one molecule of zirconium halide reacts with four molecules of a monocarboxylic acid irrespective of the nitro or amino group present and two of a dicarboxylic acid. In the case of hydroxy acids one molecule of zirconium halide reacts with only two molecules of salicylic acid showing thereby that hydrogen of both the  $\text{COOH}$  and  $\text{OH}$  groups are replaced but in the case of malic and citric acids the  $\text{OH}$  is not affected. In all the cases the halogen is completely replaced. In the case of amino acids when excess of zirconium halide is used, substitution-cum-coordination occur and chelate compounds of the following type are obtained.



Thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

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# POLAROGRAPHIC DETERMINATION OF SILVER AND MERCURY

By

G. S. DESHMUKH, A. L. J. RAO\* and N. C. V. ACHARYULU

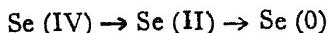
Division of Analytical Chemistry, Banaras Hindu University, Varanasi

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An indirect method for the determination of silver and mercury is given. Silver and mercury are precipitated by the addition of an excess of selenious acid or sodium selenite. The precipitates are filtered and in an aliquot of filtrate the amount of selenium is determined polarographically, in 1 M ammonium acetate. From the amount of unreacted and total selenium, the amount of selenium reacted with the metal and thence the amount of metal is determined. Twenty part per million of silver and mercury can be determined with less than one percent error.

Very few polarographic methods of determination of silver and mercury are available in literature. Silver can be determined using ammonium sulphate<sup>1</sup> as supporting electrolyte. From a solution of potassium argentocyanide<sup>2</sup>, well defined wave with a half wave potential of about 0·3 V (vs) S. C. E. is obtained. Cave and Hume<sup>3</sup> determined silver polarographically with an accuracy of 5% over a wide range. Mercury does not give a well defined polarographic wave. However, 0.1 M nitric acid, 1 M hydrochloric acid and 1 M sodium fluoride are used as supporting electrolytes<sup>4,5</sup> in which it gives a wave having a half wave potential  $\approx$  0 (vs) S. C. E. Application of selenious acid for quantitative determinations was first reported by Nauri<sup>6</sup> and is being used in these laboratories.

In recent studies<sup>7</sup> on the polarography of selenious acid and alkali selenites using 1 M ammonium acetate base electrolyte containing 0·005% gelatin (pH  $\sim$  6·2), two well defined waves with  $E_{\frac{1}{2}}$  = -0·8V and -1·33V (vs) S. C. E. have been obtained. The plot  $i_d$  (vs) C gave straight lines for both the waves upto a concentration of 3·0 mM Se (IV). Of the two waves only the first is completely reversible. However the slope of the log plot indicates that each wave corresponds to two electron change and the reduction to the metal therefore occurs in two successive steps:



The present investigation is carried out with a view to develop a rapid polarographic method for estimating silver or mercury by adding an excess of sodium selenite and drawing the polarogram of the unreacted sodium selenite.

## EXPERIMENTAL

All reagent grade chemicals were used for preparing the solutions. A Fisher Electropode in conjunction with a saturated calomel electrode was used to draw the polarogram of excess selenium. A Beckmann Zeromatic pH meter was employed for the accurate determination of pH.

Since silver or mercury does not give a wave in ammonium acetate at the dropping mercury electrode, an indirect method is developed and is made use of in present study. An aliquot of the metal solution is taken to which a known excess of sodium selenite is added and the volume is made upto 25 ml. In the case of mercury the pH of the solution is adjusted to about 6, before making up

\*Present address: Department of Chemistry, Punjabi University, Patiala,

the volume. The precipitate is allowed to stand for some time and then filtered, 5 ml of the filtrate is taken in 1 M ammonium acetate containing 0.005% gelatin and the pH of the solution is adjusted to 6.2. The polarogram of this solution is drawn. From the calibration curve of seleninm under the same conditions, the amount of selenium left behind is known. The difference being the amount of selenium reacted with the metal and hence the metal concentration is determined.

Thus very low concentrations of silver and mercury may be determined by this method. Results obtained in the present study are given.

TABLE I  
Determination of Silver

Amount of silver taken, mg.	Amount of silver found mg.	Standard Deviation
0.539	0.539	- 0.19
1.078	1.076	+ 0.01
1.617	1.615	+ 0.01
2.234	2.235	- 0.19
4.312	4.292	+ 0.31

TABLE II  
Determination of Mercury

Amount of mercury taken mg.	Amount of Mercury Found mg.	Standard Deviation
0.5416	0.5416	- 0.23
0.7221	0.7166	+ 0.33
1.2640	1.2630	- 0.13
1.8057	1.8010	+ 0.07
2.7075	2.7069	- 0.20

#### SUMMARY

An indirect polarographic method for the determination of silver and mercury is given based upon the precipitation of metal selenites and the polarographic behaviour of selenium in ammonium acetate. The method is quite rapid and accurate and small amounts of metals can be determined.

Sincere thanks of the authors are due to Professor G. B. Singh for providing the necessary facilities.

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SOME FORMULAE FOR THE ASSOCIATED LEGENDRE FUNCTION  
OF THE FIRST KIND

*Ey*

R. K. SAXENA

*Department of Mathematics, Faculty of Engineering, University of Jodhpur, Jodhpur*

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ABSTRACT

In this paper we evaluate an integral of the product of the associated Legendre function of the first kind and Meijer's G-function.

A result given earlier by Sharma (6, p. 162) follows as its particular case.

1. *Introductory.* In the present paper we evaluate an integral involving an associated Legendre function of the first kind and the G-function with the help of the Parseval-Goldstein theorem of the operational calculus (3, p. 105). The result established is of general character and a result due to Sharma (6, p. 162) follows as its particular case. From this formula some interesting integrals involving Bessel functions, Whittaker functions and MacRobert's E-functions are deduced in § 4. For the definitions, properties and the asymptotic behaviour of the G-function see 1, p. §§ 5.3, 5.3.1 and 4, § 18). In what follows  $n$  is a positive integer and

the symbol  $\Delta(n; \alpha)$  denotes the set of parameters  $\frac{\alpha}{n}, \frac{\alpha+1}{n}, \dots, \frac{\alpha+n-1}{n}$ .

2. *Formulae required in the proof.* The following infinite integral can easily be obtained from author's formula (5, p. 401, eq. 8)

$$\begin{aligned}
 & \int_0^\infty t^{\sigma-1} K_\nu(at) G_{\gamma, \delta}^{\alpha, \beta} \left( zt^n \mid \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right) dt. \\
 & = (2\pi)^{(1-A-n)} \frac{B+\sigma-1}{2} \frac{\sigma-1}{n} \frac{\sigma}{a} \\
 & \times G_{2\gamma+2n, 2\delta}^{2\alpha, 2\beta+2n} \left[ \frac{z^2 (2n)^{2n}}{a^{2n} 2^{2\delta-2\gamma}} \right. \\
 & \quad \left. \left. \Delta \left( n; \frac{2-\sigma-\nu}{2} \right), \Delta \left( n; \frac{2+\nu-\sigma}{2} \right), \frac{a_1}{2}, \frac{a_1+1}{2}, \dots, \frac{a_\gamma+1}{2} \right] , \quad (1)
 \end{aligned}$$

Where  $A = \alpha + \beta - \frac{1}{2}\gamma - \frac{1}{2}\delta$ ,  $B = \sum_{i=1}^{\delta} b_i - \sum_{i=1}^{\gamma} a_i + \frac{1}{2}\gamma - \frac{1}{2}\delta$

$R(\sigma \pm \nu + n \min b_j) > 0$  for  $j = 1, 2, \dots, \alpha$ ,  $R(a) > 0$ ,

$|\arg z| < (\alpha + \beta - \frac{1}{2}\gamma - \frac{1}{2}\delta) \pi$ ,  $\alpha + \beta > \frac{1}{2}\gamma + \frac{1}{2}\delta$ .

If  $R(\mu) < 1$ ,  $R(p) > 0$  then (2, p. 278).

$$(t^2 + 2at)^{-\frac{1}{2}\mu} P_v^\mu(1+t/a) \doteq \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} t^{\mu + \frac{1}{2}} e^{ap} K_{v+\frac{1}{2}}(ap) \quad (2)$$

If  $R[\rho + n(1-a_j)] > 0$  for  $j = 1, 2, \dots, \beta$ ,  $R(a+p) > 0$ ,

$|\arg z| < (\alpha + \beta - \frac{1}{2}\gamma - \frac{1}{2}\delta - \frac{1}{2}n) \pi$ ,  $\alpha + \beta > \frac{1}{2}\delta + \frac{1}{2}\gamma + \frac{1}{2}n$  then (5, p. 402)

$$\begin{aligned} & \frac{-ax}{x} x^{\rho-1} G_{\gamma, \delta+n}^{\alpha, \beta} \left( z/x^n \mid \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right) \\ & \doteq p(p+a)^{-\rho} (2\pi)^{\frac{1}{2}-\frac{1}{2}n} \frac{\sigma-\frac{1}{2}}{n} \\ & \times G_{\gamma, \delta}^{\alpha, \beta} \left( z(p+a)^n \mid \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right) \end{aligned} \quad (3)$$

3. *The integral.* The formula to be proved here is

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2 + 2at)^{-\frac{1}{2}\mu} P_v^\mu(1+t/a) \\ & \times G_{\gamma, \delta}^{\alpha, \beta} \left[ z(t+a)^n \mid \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right] dt. \\ & = (2\pi)^{\frac{1}{2}-A} \pi^{-\frac{1}{2}} n^{\mu-1} a^{1-\rho-\mu} \frac{2^{\mu+B-\frac{1}{2}}}{2} \\ & \times G_{2\gamma+2n, 2\delta+2n}^{2\alpha+2n, 2\beta} \left( \frac{z^2 a^{2n}}{4^{\delta-\gamma}} \right. \\ & \left. \left| \begin{matrix} \frac{a_1}{2}, \dots, \frac{a_\gamma+1}{2}, \Delta(n; \rho/2), \Delta(n; \frac{1+\rho}{2}) \\ \Delta(n; \frac{\rho+\mu-\nu}{2}), \Delta(n; \frac{\rho+\mu-\nu-1}{2}, -\frac{t_1}{2}, \dots, \frac{b_\delta+1}{2}) \end{matrix} \right. \right), \quad (4) \end{aligned}$$

This formula is valid under the following sets of conditions.

(i)  $R(1-\mu+n \min b_j) > 0$  for  $j = 1, 2, \dots, \alpha$ ;  $|\arg a| < \pi$ ,

$$R[\rho + \mu + \nu + n(1 - \max a_j)] > 0, R[\rho + \mu - \nu - 1 + n(1 - \max a_j)] > 0,$$

for  $j = 1, 2, \dots, \beta$ ,  $|\arg z| < \pi A$ ,  $A > 0$ ;

(ii)  $R(1 - \mu + n \min b_j) > 0$  for  $j = 1, 2, \dots, \alpha$ ,  $|\arg a| < \pi$ ,

$$R[\rho + \mu + \nu + n(1 - \max a_j)] > 0, R[\rho + \mu - \nu - 1 + n(1 - \max a_j)] > 0,$$

for  $j = 1, 2, \dots, \beta$ ,  $|\arg z| \leq A\pi$ ,  $A \geq 0$ ,

$$R \left[ n \left( \sum_{i=1}^{\gamma} a_i - \sum_{i=1}^{\delta} b_i - \frac{1}{2} \right) + (\delta - \gamma)(\rho + \mu - \nu - 1 + \frac{1}{2}n) \right] > -1,$$

$$R \left[ n \left( \sum_{i=1}^{\gamma} a_i - \sum_{i=1}^{\delta} b_i - \frac{1}{2} \right) + (\delta - \gamma)(\rho + \mu + \nu + n/2) \right] > -1.$$

(iii)  $\gamma > \delta$  (or  $\gamma \geq \delta$  and  $|z| < 1$ ),  $R(1 - \mu + n \min b_j) > 0$ ,

for  $j = 1, 2, \dots, \alpha$ ;  $R[\rho + \mu + \nu + n(1 - \max a_j)] > 0$ ,

$R[\rho + \mu - \nu - 1 + n(1 - \max a_j)] > 0$  for  $j = 1, 2, \dots, \beta$ ,  $|\arg a| < \pi$ .

*Proof.* If we use the operational pairs (2) and (3) in the Parseval-Goldstein theorem of Operational Calculus (3, p. 105) we see that

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_v^\mu (1+t/a) G_{\gamma, \delta}^{\alpha, \beta} \left[ z(t+a)^n \middle| \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right] dt \\ &= n^{\frac{1}{2}-\sigma} (2\pi)^{\frac{1}{2}} (n-1) \left( \frac{2a}{\pi} \right)^{\frac{1}{2}} \int_0^\infty t^{\rho+\mu-3/2} K_{v+\frac{1}{2}}(at) \\ & \quad \times G_{\gamma, \delta+n}^{\alpha, \beta} \left( \frac{z}{t^n} \middle| \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta, \Delta(n; \rho) \end{matrix} \right) dt \\ &= n^{\frac{1}{2}-\sigma} (2\pi)^{\frac{1}{2}} (n-1) \left( \frac{2a}{\pi} \right)^{\frac{1}{2}} \int_0^\infty t^{\rho+\mu-3/2} K_{v+\frac{1}{2}}(at) \\ & \quad \times G_{\delta+n, \gamma}^{\beta, \alpha} \left( \frac{t^n}{z} \middle| \begin{matrix} 1-b_1, \dots, 1-b_\delta \\ 1-a_1, \dots, 1-a_\gamma \end{matrix}, \Delta(n; 1-\rho) \right) dt \end{aligned}$$

On evaluating the integral on the right with the help of (1) and using the property of the G-function

$$G_{\gamma, \delta}^{\alpha, \beta} \left( \frac{-1}{x} \middle| \begin{matrix} a_r \\ b_s \end{matrix} \right) = G_{\delta, \gamma}^{\beta, \alpha} \left( x \middle| \begin{matrix} 1-b_s \\ 1-a_r \end{matrix} \right), \quad (5)$$

we arrive at the result.

The conditions of validity can easily be obtained on considering the asymptotic behaviour of the G-function due to Meijer (5) for different values of the parameters.

4. Particular cases. (i) If we take  $\alpha=\delta=2$ ,  $\beta=\gamma=0$ ,  $b_1=\lambda/2$ ,  $b_2=-\lambda/2$  and  $n=1$  replace  $z$  by  $z^{2/4}$  and use the formula (1, p. 216, eq. 4)

$$G_{0,2}^{2,0} \left( \frac{1}{4}x^2 \mid a, b \right) = 2(x/2)^{a+b} K_{a-b}(x), \quad (6)$$

we obtain

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_v^\mu (1+t/a) K_\lambda \left( z \sqrt{(t+a)} \right) dt \\ &= a^{1-\rho-\mu} \frac{\pi^{-1}}{2} {}_2^{(\mu-5/2)} \\ & \times G_{2,6}^{6,0} \left( \frac{a^2 z^4}{256} \mid \begin{array}{c} \rho/2, \frac{\rho+1}{2} \\ \frac{\rho+\mu+v}{2}, \frac{\rho+\mu-v-1}{2}, \frac{\lambda}{4}, \frac{\lambda+2}{4}, \frac{\lambda}{4}, \frac{2-\lambda}{4} \end{array} \right), \end{aligned} \quad (7)$$

where  $R(\mu) < 1$ ,  $R(z) > 0$  and  $|\arg a| < \pi$ .

(ii) Putting  $\alpha=1$ ,  $\delta=2$ ,  $\beta=\gamma=0$ ,  $b_1=\frac{1}{2}\lambda$ ,  $b_2=-\frac{1}{2}\lambda$ ,  $n=1$  replacing  $z$  by  $z^{2/4}$  and applying the result (1, p. 216, eq. 3),

$$G_{0,2}^{1,0} \left( \frac{1}{4}x^2 \mid a, b \right) = (\frac{1}{2}x)^{a+b} J_{a-b}(x), \quad (8)$$

it is seen that

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_v^\mu (1+t/a) J_\lambda \left[ z(t+a)^{\frac{1}{2}} \right] dt \\ &= a^{1-\rho-\mu} {}_2^{(\mu-1)} \\ & \times G_{2,6}^{4,0} \left( \frac{a^2 z^4}{256} \mid \begin{array}{c} \frac{\rho}{2}, \frac{\rho+1}{2} \\ \frac{\lambda}{4}, \frac{\lambda+2}{4}, \frac{\rho+\mu+v}{2}, \frac{\rho+\mu-v-1}{2} \end{array} \right), \end{aligned} \quad (9)$$

where  $R(\mu) < 1$ ,  $R(\rho+\mu-v) > \frac{1}{2}$ ,  $R(\rho+\mu+v) > -3/4$ ,  $|\arg z| < \pi$  and  $z$  is real and positive.

(iii) On taking  $\alpha=\delta=2$ ,  $\beta=0$ ,  $\gamma=n=1$ ,  $a_1=1-k$ ,  $b_1=\frac{1}{2}+m$ ,  $b_2=\frac{1}{2}-m$  and using the property of the G-function (1, p. 221, eq. 68),

$$G_{1,2}^{2,0} \left( x \mid \begin{array}{c} 1-k+l \\ \frac{1}{2}+m+l, \frac{1}{2}-m+l \end{array} \right) = x^l e^{-\frac{1}{2}x} W_{k,m}(x), \quad (10)$$

it follows that

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_v^\mu (1+t/a) \exp \{ -\frac{1}{2}z(t+a) \} W_{k,m} [z(t+a)] dt. \\ & = \pi^{-\frac{1}{2}} a^{1-\rho-\mu} 2^{\mu+k-1} \\ & \times G_{4,6}^{6,0} \left( \frac{a^2 z^2}{16} \left| \begin{array}{c} \frac{1-k}{2}, \frac{2-k}{2}, \frac{1}{2}\rho, \frac{1}{2}+\frac{1}{2}\rho \\ \frac{1}{2}(\rho+\mu+\nu), \frac{1}{2}(\rho+\mu-\nu-1), \frac{1\pm 2m}{2}, \frac{3\pm 2m}{2} \end{array} \right. \right), \quad (11) \end{aligned}$$

where  $R(\mu) < 1$ ,  $|\arg a| < \pi$ ,  $R(z) > 0$ .

(iv) Similarly if we put  $\alpha=\delta=2$ ,  $\beta=\gamma=1$ ,  $n=1$ ,  $a_1=1-k$ ,  $b_1=\frac{1}{2}-m$ ,  $b_2=\frac{1}{2}+m$  and use the formula (1, p. 221, eq. 69.)

$$G_{1,2}^{2,1} \left( z \left| \begin{array}{c} 1+k+l \\ \frac{1}{2}-m+l, \frac{1}{2}+m+l \end{array} \right. \right) = \Gamma(\frac{1}{2}-k \pm m) e^{\frac{1}{2}z} W_{k,m}(z), \quad (12)$$

we find that

$$\begin{aligned} & \int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_v^\mu (1+t/a) \exp \{ \frac{1}{2}z(t+a) \} W_{k,m} [z(t+a)] dt. \\ & = \frac{1}{\pi} a^{1-\rho-\mu} 2^{\mu-k-2} \\ & \times G_{4,6}^{6,2} \left( \frac{a^2 z^2}{16} \left| \begin{array}{c} \frac{1+k}{2}, \frac{2+k}{2}, \frac{\rho}{2}, \frac{\rho+1}{2} \\ \frac{\rho+\mu+\nu}{2}, \frac{\rho+\mu-\nu+1}{2}, \frac{1\pm 2m}{4}, \frac{3\pm 2m}{4} \end{array} \right. \right), \quad (13) \end{aligned}$$

where  $R(\mu) < 1$ ,  $R[\rho+\mu-\nu-k-1] > 0$ ,  $R(\rho+\mu+\nu-k) > 0$ ,  $|\arg a| < \pi$

and  $|\arg z| < \frac{3\pi}{2}$ .

(v) Lastly if we take  $\alpha=l$ ,  $\beta=1$ ,  $\gamma=m+1$ ,  $\delta=l$ ,  $a_1=1$ , write  $b_j$  and  $a_i$  for the parameters  $a_{j+1}$  and  $b_i$  respectively ( $j=1, 2, \dots, m$  and  $i=1, 2, \dots, l$ ) and use the formula (1, p. 215.)

$E(l; a_r : m ; b_s ; x)$

$$= G_{m+1, l}^{l, 1} (x | \begin{array}{c} 1, b_1, \dots, b_m \\ a_1, \dots, a_l \end{array}), \quad (14)$$

then it is found that

$$\int_0^\infty (t+a)^{-\rho} (t^2+2at)^{-\frac{1}{2}\mu} P_\nu^\mu (1+t/a) \times E[l; a_r : m ; b_s : z(t+a)^n] dt.$$

$$= (2\pi)^{\frac{1}{2}(m-l)} \pi^{-\frac{1}{2}} n^{\mu-1} a^{l-\rho-\mu} 2^{\mu+\sum_{i=1}^l a_i - \sum_{j=1}^m b_j + \frac{1}{2}(m-l)-1}$$

$$\times G_{2m+2n+2, 2l+2n} \left( \frac{z^2 a^{2n}}{2^{2(l-m-1)}} \right| \begin{array}{l} \frac{1}{2}, 1, \frac{b_1}{2}, \frac{b_1+1}{2}, \dots, \frac{b_m+1}{2}, \Delta(n; \rho/2), \Delta\left(n; \frac{1+\rho}{2}\right) \\ \Delta\left(n; \frac{\rho+\mu+\nu}{2}\right), \Delta n; \left(\frac{\rho+\mu-\nu-1}{2}\right), \frac{a_1}{2}, \dots, \frac{a_l+1}{2} \end{array} , (15)$$

where  $R(\mu) < 1$ ,  $R(\rho+\mu-\nu-1) > 0$ ,  $R(\rho+\mu+\nu) > 0$

$|\arg a| < \pi$ ,  $|\arg z| < \frac{1}{2}(l-m+1)\pi$ ,  $l > m+1$

For  $n=1$  (15) reduces to a result given by Sharma (6, p. 162)

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# ON THE SUPERPOSITION OF QUANTUM STATES

By

R. L. DASVARMA

*Department of Mathematics, L. S. College, Muzaffarpur*

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## ABSTRACT

In the usual formulation of Quantum Theory the superposition principle appears as a consequence of the wave-particle dualism, introduced as a basic law of nature. In this paper the superposition principle has been deduced from a simple correlation law among the probabilities of transition between different quantum states. This correlation law is based on symmetry, invariance and transitivity.

The representation of the states by Hilbert vectors and the correspondence between the inner products of these vectors and the transition probabilities have been shown to follow as consequences of the correlation law.

1. Recently, Lande<sup>1</sup> has formulated a simple correlation law for the probabilities of transition among the various states of a system. This law, based on simple considerations of symmetry, transitivity and invariance, is the multiplication of unitary matrices. In this paper, it has been shown that the principle of superposition of states which is regarded as fundamental by the founders of quantum theory, such as Dirac,<sup>2</sup> can be deduced from Lande's correlation law, without any appeal to wave-particle dualism. Further, the representation of quantum states by Hilbert vectors, treated as an axiom in the mathematical formulation of the theory is a natural consequence of the correlation law.

2. Let, A, B, C, ..... be the various observables (i. e. measurable physical quantities) pertaining to a physical system and let  $A_i$ ,  $i = 1, 2, \dots$ ;  $B_j$ ,  $j = 1, 2, \dots$ ;  $C_k$ ,  $k = 1, 2, \dots$  denote the various states of the system in which these observables have the different possible values  $\alpha_i$ ,  $\beta_j$ ,  $\gamma_k$ , ...., respectively. Lande's method consists in setting up the various probability tables  $P_{AB}$ ,  $P_{AC}$ ,  $P_{BC}$ , ..., where

$$(2\cdot1) \quad P_{AB} = \begin{pmatrix} P(A_1 \rightarrow B_1) & P(A_1 \rightarrow B_2) & \dots \\ P(A_2 \rightarrow B_1) & P(A_2 \rightarrow B_2) & \dots \\ \dots & \dots & \dots \end{pmatrix}$$

with  $P(A_i \rightarrow B_j)$  denoting the transition probability from the state  $A_i$  to the state  $B_j$ , i. e. the probability of obtaining the value  $\beta_j$  for the observable B on measurement when the system is in the state  $A_i$ . Evidently, for a given state  $A_i$ ,

$$(2\cdot2) \quad \sum_j P(A_i \rightarrow B_j) = 1.$$

On account of the classical principle of reversibility of processes, Lande<sup>1</sup> assumes a symmetry between  $(A_i \rightarrow B_j)$  and  $(B_j \rightarrow A_i)$  and puts

$$(2\cdot3) \quad P(A_i \rightarrow B_j) = P(B_j \rightarrow A_i).$$

Since we must also have  $\sum_i P(B_j \rightarrow A_i) = 1$ ,

$$(2\cdot4) \quad \sum_i P(A_i \rightarrow B_j) = 1.$$

Thus  $P_{BA} = P_{AB}^T$ , the transpose of  $P_{AB}$ , and  $P_{AB}$  is a square array, generally infinite, with the sum of each row and each column equal to unity.

On account of the reproducibility of states,

$$(2.5) \quad P(A_i \rightarrow A_j) = \delta_{ij},$$

showing that  $P_{AA}$  has the form of a unit matrix.

3. In seeking a correlation law among three P-tables,  $P_{AB}$ ,  $P_{BC}$  and  $P_{AC}$ , Lande' found that a simple law among them consistent with the above conditions is not possible. However, if one makes the assumption.

$$(3.1) \quad P(A_i \rightarrow B_j) = |\psi(A_i \rightarrow B_j)|^2,$$

$$(3.2) \quad \psi(B_j \rightarrow A_i) = \psi^*(A_i \rightarrow B_j),$$

$$(3.3) \quad \psi(A_i \rightarrow A_j) = \delta_{ij},$$

one finds that a correlation law among  $\psi_{AB}$ ,  $\psi_{BC}$ ,  $\psi_{CA}$  is possible, where  $\psi_{AB}$  is the square array of the complex numbers  $\psi(A_i \rightarrow B_j)$ . This substructure for the P-tables is the law of multiplication for the matrices. From their very definition, the  $\psi$ -matrices are unitary. We have for the correlation law,

$$(3.4) \quad \psi_{AC} = \psi_{AB} \cdot \psi_{BC}, \quad \psi_{AB} \cdot \psi_{BA} = 1, \quad \psi_{AA} = 1,$$

$$(3.5) \quad \psi(A_i \rightarrow C_k) = \sum_j \psi(A_i \rightarrow B_j) \psi(B_j \rightarrow C_k).$$

4. If the observable B can take on a continuous range of values, we have to consider the density of probability instead of probability distributions. The density functions are continuous functions  $p(A_i \rightarrow \beta)$  of the continuous random variable B and  $p(A_i \rightarrow \beta) d\beta$  is the probability that when the system is in the state  $A_i$ , a measurement of B will yield the value between  $\beta$  and  $\beta + d\beta$ . The  $\psi$ -matrix will also be replaced by a set of continuous functions  $\{\psi_i(\beta; A)\}$  where

$$(4.1) \quad p(A_i \rightarrow \beta) = |\psi_i(\beta; A)|^2, \quad \int |\psi_i(\beta; A)|^2 d\beta = 1.$$

If C be an observable having only a discrete set of values, corresponding to (3.5), we now have

$$(4.2) \quad \psi(A_i \rightarrow C_k) = \int \psi_i(\beta; A) \psi_k^*(\beta; C) d\beta.$$

If on the other hand, C has a continuous range of values  $\gamma$ ,  $\psi(A_i \rightarrow C_k)$  has to be replaced by the continuous function  $\psi_i(\gamma; A)$  and we have

$$(4.3) \quad \psi_i(\gamma; A) = \int \psi_i(\beta; A) \psi^*(\beta, \gamma) d\beta = \int \psi(\gamma, \beta) \psi_i(\beta; A) d\beta.$$

The transition from the discrete-valued index function to the continuous function of a continuous variable is effected through replacements of summation by integrals. The unitarity conditions

$$(4\cdot4) \quad \sum_j \psi(A_i \rightarrow B_j) \psi^*(B_j \rightarrow A_k) = \psi(A_i \rightarrow A_k) = \delta_{ik}$$

is replaced in this case by

$$(4\cdot5) \quad \int \psi_i(\beta; A) \psi_k^*(\beta; A) d\beta = \psi(A_i \rightarrow A_k) = \delta_{ik},$$

$$(4\cdot6) \quad \int \psi(\gamma, \beta) \psi^*(\gamma', \beta) d\beta = \psi(\gamma, \gamma') = \delta(\gamma - \gamma')$$

where  $|\psi(\gamma, \gamma')|^2$  is the density of probability for C having the value  $\gamma'$ , when the system is in the state such that C has the value  $\gamma$ , and  $\delta(\gamma - \gamma')$  is the delta function of Dirac.

5. We can define the state in which A has the value  $a_i$  (i. e. the state  $A_i$ ) through the probabilities  $P(A_i \rightarrow B_j)$ , for all  $j$ , or better, (since the correlation law is stated for the  $\psi$ 's) through the set  $\{\psi(A_i \rightarrow B_j)\}$ , which may be said to represent the state  $A_i$ . The same state  $A_i$  can also be represented by the set  $\{\psi(A_i \rightarrow C_k)\}$  for all  $k$ . In the case when B and C have continuous range of values, the sets  $\{\psi(A_i \rightarrow B_j)\}$ ,  $\{\psi(A_i \rightarrow C_k)\}$  are replaced by the continuous functions  $\psi_i(\beta; A)$  and  $\psi_i(\gamma; A)$ . Equations (3·5), (4·2) and (4·3) are then equations of transformation of representations of the same state  $A_i$ . These representations, we shall call the B-representation and C-representation of the state  $A_i$ . These equations together with the equations (4·4), (4·5) and (4·6) show that the transformations correspond to unitary transformations, respectively in the Hilbert spaces  $L_2$  of vectors and  $L_2$  of square-integrable functions. Further,  $\psi(A_i \rightarrow C_k)$  has the form of the inner product of two vectors and  $\psi(B_i \rightarrow B_j)$  and  $\psi(\beta, \beta')$  represent the inner product of orthogonal vectors in these spaces.

6. We can summarise the above results as follows:—

(i) Every state of a system can be represented by a vector in Hilbert space.

(ii) the inner product of two vectors representing two states is such that the square of its absolute value is the probability of transition from one state to the other.

(iii) two states are represented by orthogonal vectors if the probability of transition between them is zero.

(iv) Since the probability  $P(A_i \rightarrow A_i) = 1$ , the vectors representing states are of unit norm (this condition does not always hold for vectors in the space  $L_2$ ).

(v) The condition  $P(A_i \rightarrow A_j) = \delta_{ij}$  signifies that the vectors representing the various states  $A_i$ , characteristic of the observable A (i. e., for which A has well-defined values) form an orthonormal set and since no other state X satisfies the

condition  $P(X \rightarrow A_i) = 0$  for all  $i$ , this orthonormal set is complete and form a basis of representation in the Hilbert space of state vectors. Any state  $X$  can be represented as the linear combination

$$(6'1) \quad X = \sum_i (X, A_i) A_i,$$

where  $(X, A_i)$  is the inner product of the vectors representing the states  $X$  and  $A_i$  and  $| (X, A_i) |^2 = P(X \rightarrow A_i)$ . Deduction (i) is the first axiom in an axiomatic formulation of quantum theory and (6'1) is the mathematical formulation of the principle of superposition.

We have, here, deduced both as consequences of a simple metric law for probabilities.

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# EFFECT OF ORGANIC SUBSTANCES ON NITRIFICATION BY NITROSOMONAS—PART I

By

S. P. TANDON and R. C. RASTOGI

*Chemistry Department, University of Allahabad, Allahabad (U. P.,)*

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## ABSTRACT

The effect of D-glucose and D-fructose on the nitrite formation by Nitrosomonas has been studied. The experimental results indicate that the above two sugars in proper amounts are not toxic to the bacteria, as has been so far believed but on the other hand serve as better food material and stimulate their growth.

After the first isolation of the nitrite forming bacteria, Nitrosomonas, by Winogradsky<sup>1</sup>, it was observed very early that the addition of organic food material, like sugars, slowed the process of nitrite formation both in soil as well as in culture solutions. This inhibitory effect of organic matter on nitrification was subsequently confirmed by a large number of investigators, but the cause of this inhibitory effect still remains unexplained.

In order to understand the influence of organic food material on nitrite formers, we have carried out extensive experiments with Nitrosomonas in the presence of different organic compounds. The results obtained with D-glucose and D-fructose are reported here.

## EXPERIMENTAL

### *Isolation of Nitrosomonas*

A pure culture of nitrite forming bacteria, Nitrosomonas, was prepared from the garden soil by Omeliansky's method of elective culture. The composition of the medium is as follows :—

Ammonium sulphate	... 2·5 gms.
Potassium hydrogen phosphate	... 1·0 gm.
Magnesium sulphate	... 0·5 gm.
Sodium chloride	... 2·0 gm.
Ferrous sulphate	... 0·4 gm.
Distilled water	... 1 litre
Magnesium carbonate	... excess (0·5 gm in 50 ml.)

50 ml portions of the above medium were taken in 250 ml Jena-glass conical flasks which were plugged with absorbent cotton. These were sterilized at 15 pounds pressure for half an hour in an autoclave. The ammonium sulphate solution was sterilized separately. Later, all the flasks were left for cooling. 1 ml of the above sterilized ammonium sulphate was then added to each of the conical flasks containing the other constituents of the medium. The addition was made with a sterilized pipette, the top end of which was plugged with absorbent cotton.

After the addition of the ammonium sulphate solution about one gram of good garden soil was added into one of the flasks which was the incubated at 35°C. After about a week, the growth of the organism started. This was indicated

by the appearance of nitrite and the disappearance of ammonium sulphate. When all the ammonium sulphate had been oxidised to nitrite a fresh portion of the ammonium sulphate solution was added. This second portion was oxidised much more rapidly, since the nitrite forming bacteria by then had developed abundantly. After several additions of the ammonium sulphate solution a vigorous culture of the specific organism was obtained. A drop of the suspension from the bottom of the flask was then transferred to another flask containing the same sterilised medium. After 4 or 5 such transfers, the culture obtained was fairly pure and rich enough in the specific organism, and was used for the isolation purpose.

The following silicic acid medium was used for the isolation of the nitrite forming bacteria.

Equal volumes of clear sodium silicate (sp. gr. 1·05 to 1·06) and hydrochloric acid (sp. gr 1·1) were mixed by pouring the first into the second ; the mixture was then dialysed for several days in distilled water, which was changed twice daily. When the solution was free from chloride ions it was sterilized in an autoclave for 15 minutes at 15 pounds pressure. In addition to silicic acid sol the following four solutions were prepared :

- |   |             |
|---|-------------|
| (1) Ammonium sulphate   | ... 3 gms.  |
| Potassium Hydrogen phosphate  | ... 1 gm.   |
| Magnesium sulphate  | ... 0·5 gm. |
| Distilled water   | ... 100 ml. |
| (2) Two per cent solution of ferrous sulphate.  |             |
| (3) Saturated sodium chloride solution.   |             |
| (4) Milk of magnesia, a thick suspension of finely powdered magnesium carbonate in distilled water. |             |

50 ml of the silicic acid sol was placed in a flask, then 2·5 ml of solution (1) were added and 1 ml of solution (2). Enough milk of magnesia was added to give the mixture a milky appearance. The mixture was then poured, with constant stirring into sterile, small, thin walled petri-dishes (diam. about 3½ inches). Finally, one drop of the solution (3) was placed in the centre of each plate and all the dishes were then left over night in an horizontal position. The liquid solidified to a gel and a good solid medium was obtained.

In order to get the culture absolutely pure a drop of the sediment from the bottom of the flask containing the enriched bacterial culture was placed on the surface of the gel and spread over the surface with the tip of a sterile glass rod. The dishes were incubated in an inverted position at a temperature of 35°C. The colonies developed after about 15 days and a single selected colony was picked up and introduced into a fresh medium. The culture of the bacteria thus obtained was quite pure.

An examination of the bacterial sediment in a hanging drop showed motile microbes having ellipsoidal appearance. The culture thus consisted of Nitroso-monoas group of bacteria.

For the systematic study of the effect of sugars, on the organism thus isolated the following procedure was adopted. Various sets of experiments were arranged :

Solutation A—10% sterilized ammonium sulphate.

Solution B—Containing all the constituents of the Omeliansky's medium excepting ammonium sulphate.

80 ml portions of the solution B were taken in several 250 ml Jena-glass conical flasks and 0·7 gram of magnesium carbonate was added to each of the flasks. Eight sets, each comprising of eleven such flasks, were prepared having the same volume of Omeliansky's medium. The following different amounts of sugars (or the organic compound to be used) were added respectively to the ten flasks of each set—5, 10, 20, 25, 30, 40, 50, 60, 80 and 100 mg. The eleventh flask of each set was left as such with no sugar (as control). All the flasks were then sterilized at 15 pounds pressure in an autoclave for half an hour. The 10% solution of ammonium sulphate was sterilized separately in another flask and 1 ml of this sterilized solution was then added to each of the flasks. Then, 1 ml of a strong suspension of the culture medium containing the nitrite former was added to each of the flasks of the six sets with a sterilized pipette having absorbent cotton at the upper end. The culture was freed in the beginning from the traces of nitrite by repeated washing and decanting with sterilized distilled water. To carry out the control experiments under similar condition but containing no bacteria, the flasks of the seventh and eighth sets were left as such with no addition of the nitrite forming bacteria. Then, all the flasks except the flasks of the first set were incubated at the temperature of 35°C. The first set was left for the estimation of the initial amount of the total nitrogen contained in the medium.

The two sets (second and third) were employed for estimating the nitrite formed while the other two sets (fourth and fifth) for the estimation of sugars, and the mean of the two results obtained with the two similar flasks in each case was always taken. The flasks of the sixth set were employed for the estimation of the total nitrogen present in the medium after the experiment was over. The formation of nitrite was taken to be directly proportional to the activity of the organism.

#### *Estimation of Nitrite.*

The amount of the nitrite formed was estimated colorimetrically with a Duboscq colorimeter using a mixture of 0·8 per cent solution of sulphanilic acid in acetic acid of specific gravity 1·04 and 0·5 per cent solution of  $\alpha$ -naphthylamine in acetic acid of the same specific gravity as the indicator (colorimetric determination according to Griess-Ilosovay method).

The strength of the standard nitrite solution to be used in the Griess-Ilosovay method should be near about N/75000, for the indicator employed in this method is very sensitive and if higher concentration of the nitrite solution is used the colour developed is so intense that the comparison of the tinge in the colorimeter can not be done with accuracy.

The nitrite solution was standardised by titrating it against standard solution of potassium permanganate.

#### *Estimation of Total Nitrogen.*

The total nitrogen was estimated by the Kjeldahl's method as modified by Treadwell and Hall (salicylic acid reduction method)<sup>2</sup>.

#### *Estimation of Sugars.*

The estimation of aldose sugars was made by the method suggested by J. R. Collins<sup>3</sup>.

Fructose was estimated by Singh and Ghosh's method<sup>4</sup>. In this method the sugar is oxidised by alkaline copper sulphate in the presence of sodium citrate. The cuprous oxide thus obtained is then estimated iodometrically.

TABLE No. 1A

Nitrosification in the presence of D-glucose.

(i) Volume of the culture medium taken = 80 ml.

(ii) Volume of the enriched culture (inoculum) added = 1 ml.

(iii) Volume of the ammonium sulphate (10% sol.) added = 1 ml.

No.	Amount of D-glucose added to the medium (in mg.)	Amount of D-glucose left at different intervals of time					
		48	96	144	192	240	288
1	Control	Nil	Nil	Nil	Nil	Nil	Nil
2	5.00	,"	,"	,"	,"	,"	,"
3	10.00	4.374	,"	,"	,"	,"	,"
4	20.00	10.935	4.374	,"	,"	,"	,"
5	25.00	17.496	8.748	3.645	,"	,"	,"
6	30.00	19.683	12.369	5.103	,"	,"	,"
7	40.00	29.160	24.057	9.447	2.916	,"	,"
8	50.00	34.263	28.43	9.447	2.916	,"	,"
9	60.00	48.843	45.198	27.702	10.935	3.645	,"
10	80.00	71.442	67.797	50.301	29.89	16.038	6.561
11	100.00	97.686	92.580	71.44	52.488	40.09	19.683
							5.103

Control = Containing no glucose.

TABLE 1B

## Nitrosification in the presence of D-glucose.

Volume of the culture medium taken = 80 ml

Volume of the enriched culture (inoculum) added = 1 ml.

Volume of the ammonium sulphate added = 1 ml.

No.	Amount of D-glucose added to the medium (in mg)	Nitrite formed at Different Intervals of Time (mg/litre)					
		48	96	144	192	240	288
1	Control	2.852	5.308	8.845	38.336	69.00	141.542
2	5.00	...	3.412	6.900	33.120	88.458	172.55
3	10.00	...	2.203	4.600	24.150	67.896	164.26
4	20.00	...	...	2.300	10.455	28.750	74.432
5	25.00	...	...	1.564	7.0776	24.150	57.50
6	30.00	...	...	1.564	4.436	19.168	53.038
7	40.00	...	...	...	2.116	10.435	28.75
8	50.00	...	...	...	1.106	6.789	10.455
9	60.00	...	...	...	...	1.840	9.20
10	80.00	...	...	...	...	...	46.00
11	100.00	...	...	...	...	3.680	18.547
					...	...	4.600

Control = Containing no glucose.

TABLE No. 2A

## Nitrosification in the presence of D-Fructose

- (1) Volume of the culture medium taken = 80 ml  
 (2) Volume of the enriched culture (inoculum) added = 1 ml  
 (3) Volume of the ammonium sulphate added = 1 ml

No.	Amount of D-Fructose added to the medium (in mg)	Amount of D-Fructose left at different intervals of time					
		48	96	144	192	240	288
1	Control	Nil	Nil	Nil	Nil	Nil	Nil
2	5.00	"	"	"	"	"	"
3	10.00	4.374	"	"	"	"	"
4	20.00	11.664	4.374	"	"	"	"
5	25.00	14.58	6.561	"	"	"	"
6	30.00	21.87	12.383	5.103	"	"	"
7	40.00	34.99	19.68	5.103	"	"	"
8	50.00	41.55	24.057	11.664	5.103	"	"
9	60.00	53.219	39.336	20.41	9.477	"	"
10	80.00	71.44	52.49	37.908	19.68	7.29	"
11	100.00	92.583	77.274	56.86	32.076	18.225	8.019

Control = Containing no fructose.

TABLE No. 2B

## Nitrosification in the presence of D-fructose

- (1) Volume of the culture medium taken = 80 ml.  
 (2) Volume of the enriched culture (inoculum) added = 1 ml.  
 (3) Volume of the ammonium sulphate added = 1 ml.

No.	Amount of D-fructose added to the medium (in mg)	Nitrite formed at different intervals of times (mg/litre)					
		Time in Hours					
	48	96	144	192	240	288	336
1	Control	2.760	8.28	12.278	38.387	63.25	180.638
2	5.00	1.1040	5.227	16.426	69.00	140.576	222.87
3	10.00	...	2.300	6.808	31.436	64.400	268.364
4	20.00	...	1.1040	4.763	15.681	26.137	314.364
5	25.00	...	...	2.392	10.574	23.966	76.32
6	30.00	...	...	1.380	6.049	18.216	55.20
7	40.00	...	...	1.380	5.2064	7.429	153.64
8	50.00	...	...	0.9200	4.140	6.90	38.336
9	60.00	...	...	...	2.116	4.14	105.742
10	80.00	...	...	...	...	1.380	27.60
11	100.00	...	...	...	...	...	79.088
						...	19.165
						...	53.038
						...	26.818
						...	9.20
						...	2.60
						...	10.120

Control = Containing no fructose

#### DISCUSSION OF RESULTS

As is clear from the Table No. 1B, with 5 mg of glucose there was no nitrite formed in the first 48 hours but after 96 hours a fair amount of nitrite had been formed although at this stage it was less than that formed in the control experiment (no sugar). The rate of nitrite formation gradually increased and after 336 hours the amount formed became even greater than that in the control. With 10 mg of glucose similar result was obtained and after 336 hours the amount of nitrite formed was even more than with 5 mg. With different amounts of glucose up to 100 mg, it was found that the nitrite formation in every case did take place although the time lag for the nitrite formation to begin increased with the increased amounts of glucose taken initially.

The above results indicate that the bacteria utilise the sugars in the beginning as food and that after the sugars have been consumed they begin to derive energy for their growth and metabolism from the oxidation of ammonium sulphate to nitrite. It is thus clear that the nitrite formation in the presence of sugars does not take place in the beginning not because sugars are toxic but because sugars are being utilised by bacteria as food and consequently they do not need to oxidise ammonium salts to get energy for their requirements.

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# ON THE SUMS OF CERTAIN GENERALISED HYPERGEOMETRIC SERIES

*B. P.*

H. M. SRIVASTAVA

*Department of Mathematics, University of Jodhpur, Jodhpur*

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## ABSTRACT

Special values of Appell's  $F_4$  at  $x = y = 1/4$  and  $-2x = y = 1$  have been obtained, and that of a nearly-poised  ${}_3F_2(-1/8)$  has been deduced. Besides, the triple series for Lauricella's  $F_D$  and Saran's  $F_F$ ,  $F_K$ ,  $F_N$  and  $F_R$  have been summed, in terms of gamma functions, at various points.

## 1. INTRODUCTION

Appell [1, p. 22] proved that

$$(1.1) \dots F_1(\alpha, \beta, \beta'; \gamma; 1, 1) = \frac{\Gamma(\gamma)}{\Gamma(\gamma - \alpha)} \frac{\Gamma(\gamma - \alpha - \beta - \beta')}{\Gamma(\gamma - \beta - \beta')},$$

$$[\Re(\gamma - \alpha - \beta - \beta') > 0];$$

thus showing that the series for the double hypergeometric function  $F_1$  can be summed in terms of gamma functions when  $x = y = 1$ . The values of  $F_2$  and  $F_3$  at the point  $x = y = 1$  have been recently given by Pandey [5]. The latter has also summed certain hypergeometric series in three variables defined by Saran [6, pp. 77-8].

In §2 of this paper I have given in the form of lemmas the values of the fourth type of Appell's function at  $x = y = 1/4$  and when  $-2x = y = 1$ . It is interesting to note that one of these lemmas yields the sum of a nearly-poised  ${}_3F_2(-1/8)$ , which I have obtained in §3.

Series for the hypergeometric functions of three variables, namely  $F_K$ ,  $F_N$  and  $F_R$ , have been summed in §4 when  $x = y = z = 1$ , and the value of the function  $F_F$  for  $-(1/4)x = y = z = 1$  has been given in §5 in two forms. The series for Lauricella's  $F_D$  [4] has also been summed in §5 when  $x = y = 1$  and  $z = -1$  or  $\frac{1}{2}$ . These functions have been dealt with in two different sections because while the functions  $F_K$ ,  $F_N$  and  $F_R$  can be expressed as infinite series involving products of Gauss's  ${}_2F_1$ , the functions  $F_F$  and  $F_D$  are expressible in terms of  $F_1$ .

Lastly, it may be pointed out that since the functions chosen in §4 are not as symmetrical in parameters as Lauricella's functions [4], the results obtained are not as simple in form as the sum of Lauricella's  $F_D$  at the point  $(1, 1, -1)$ , which I have given in §5.

## 2. THE SUMS OF $F_4$

In this section I give the values of Appell's function  $F_4$  at  $(1/4, 1/4)$  and also when  $-2x = y = 1$ . The results are in the form of lemmas.

### LEMMA 1

$$F_4(\alpha, \beta; \gamma, \gamma'; 1/4, 1/4) = \frac{\Gamma(1/2\gamma) \Gamma(1/2 + 1/2\gamma) \Gamma(1 - 1/2\gamma) \Gamma(3/2 - 1/2\gamma)}{\Gamma(1/2\gamma + 1/2\alpha) \Gamma(1/2 + 1/2\gamma - 1/2\alpha) \Gamma(1 + 1/2\alpha - 1/2\gamma) \Gamma(3/2 - 1/2\gamma - 1/2\alpha)},$$

provided that  $\gamma + \gamma' = 1 + \alpha + \beta = 2$ .

### LEMMA 2

$$F_4[\alpha, 1 - \alpha; 2\alpha, 2(1 - \alpha); -1/2, 1] = \frac{\Gamma(2\alpha) \Gamma(1 - \alpha) \Gamma(1 + 1/2\alpha) \Gamma(3/2 - \alpha)}{\Gamma(3/2\alpha) \Gamma(1 + \alpha) \Gamma(1 - 1/2\alpha) \Gamma(3/2 - 3/2\alpha)}.$$

### Proof of the lemmas.

We know that [2, §2]

$$(2 \cdot 1) \dots F_4[\alpha, \beta; \gamma, \alpha + \beta - \gamma + 1; z(1 - Z), Z(1 - z)] = {}_2F_1(\alpha, \beta; \gamma; z) {}_2F_1(\alpha, \beta; \alpha + \beta - \gamma + 1; Z),$$

this formula being valid inside simply-connected regions surrounding  $z=0, Z=0$  for which

$$|z(1 - Z)|^{1/2} + |Z(1 - z)|^{1/2} < 1.$$

Lemma 1 follows if we use the relation [3, p. 104]

$$(2 \cdot 2) \dots {}_2F_1(a, 1 - a; c; 1/2) = \frac{\Gamma(1/2c) \Gamma(1/2 + 1/2c)}{\Gamma(1/2c + 1/2a) \Gamma(1/2 + 1/2c - 1/2a)};$$

while if we apply both [3, p. 104]

$$(2 \cdot 3) \dots {}_2F_1(a, b; 1 + a - b; -1) = \frac{\Gamma(1 + a - b) \Gamma(1 + 1/2a)}{\Gamma(1 + a) \Gamma(1 + 1/2a - b)}$$

and (2·2), we shall obtain Lemma 2.

## 3. THE SUM OF A NEARLY POSIED ${}_2F_1(-1/8)$

The function  $F_4$  can be expressed as

$$(3 \cdot 1) \dots F_4(\alpha, \beta; \gamma, \gamma'; x, y) = \sum_{m=0}^{\infty} \frac{(\alpha, m)(\beta, m)}{(1, m)(\gamma, m)} {}_2F_1(\alpha + m, \beta + m; \gamma'; y)^m.$$

Applying the relation [3, p. 104]

$$(3 \cdot 2) \dots {}_2F_1(a, b; c; 1) = \frac{\Gamma(c) \Gamma(c - a - b)}{\Gamma(c - a) \Gamma(c - b)},$$

we get

$$(3 \cdot 3) \dots {}_4F_3 (\alpha, \beta; \gamma, \gamma'; x, 1) = \frac{\Gamma(\gamma') \Gamma(\gamma' - \alpha - \beta)}{\Gamma(\gamma' - \alpha) \Gamma(\gamma' - \beta)} \times \\ \times {}_4F_3 \left[ \begin{matrix} \alpha, \beta, 1 - \gamma' + \alpha, 1 - \gamma' + \beta; \frac{1}{4}x \\ \gamma, \frac{1}{2} - \frac{1}{2}\gamma' + \frac{1}{2}\alpha + \frac{1}{2}\beta, 1 - \frac{1}{2}\gamma' + \frac{1}{2}\alpha + \frac{1}{2}\beta \end{matrix} \right].$$

Now, using Lemma 2 of the preceding section we obtain

$$(3 \cdot 4) \dots {}_3F_2 \left[ \begin{matrix} \alpha, 1 - \alpha, 3\alpha - 1; -1/8 \\ 2\alpha, \alpha + \frac{1}{2} \end{matrix} \right] \\ = \frac{\Gamma(2\alpha) \{ \Gamma(1 - \alpha) \}^2 \Gamma(2 - 3\alpha)}{\Gamma(3/2\alpha) \Gamma(1 + \alpha) \Gamma(2 - 2\alpha)} \frac{\Gamma(1 + \frac{1}{2}\alpha)}{\Gamma(1 - 2\alpha)} \frac{\Gamma(3/2 - \alpha)}{\Gamma(1 - \frac{1}{2}\alpha) \Gamma(3/2 - 3/2\alpha)}.$$

#### 4. THE SUMS OF $F_K$ , $F_N$ AND $F_R$

The function

$$(4 \cdot 1) \dots F_K (\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3; \gamma_1, \gamma_2, \gamma_3; x, y, z)$$

$$= \sum_{p=0}^{\infty} \frac{(\alpha_2, p)(\beta_1, p)}{(1, p)(\gamma_3, p)} {}_2F_1 (\alpha_1, \beta_1 + p; \gamma_1; x) {}_2F_1 (\alpha_2 + p, \beta_2; \gamma_2; y) z^p.$$

Now, using the formula (3.2) we get

$$(4 \cdot 2) \dots F_K (\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3; \gamma_1, \gamma_2, \gamma_3; 1, 1, z)$$

$$= \frac{\Gamma(\gamma_1) \Gamma(\gamma_2)}{\Gamma(\gamma_1 - \alpha_1) \Gamma(\gamma_2 - \alpha_2)} \frac{\Gamma(\gamma_1 - \alpha_1 - \beta_1)}{\Gamma(\gamma_1 - \beta_1)} \frac{\Gamma(\gamma_2 - \alpha_2 - \beta_2)}{\Gamma(\gamma_2 - \beta_2)} \times \\ \times {}_4F_3 \left[ \begin{matrix} \alpha_2, \beta_1, 1 - \gamma_1 + \beta_1, 1 - \gamma_2 + \alpha_2; z \\ \gamma_3, 1 - \gamma_1 + \alpha_1 + \beta_1, 1 - \gamma_2 + \alpha_2 + \beta_2 \end{matrix} \right].$$

On applying the relation [3, p. 197]

$$(4 \cdot 3) \dots {}_4F_3 \left[ \begin{matrix} a, 1 + \frac{1}{2}a, d, e; -1 \\ \frac{1}{2}a, 1 + a - d, 1 + a - e \end{matrix} \right] = \frac{\Gamma(1 + a - d) \Gamma(1 + a - e)}{\Gamma(1 + a) \Gamma(1 + a - d - e)},$$

we obtain

$$(4 \cdot 4) \dots F_K (\alpha_1, \alpha_2, \alpha_3, 1 + \frac{1}{2}\alpha_2, \beta_2, 1 + \frac{1}{2}\alpha_2; 3/2 + \frac{1}{2}\alpha_1, \frac{1}{2} + \frac{1}{2}\alpha_2 + \frac{1}{2}\beta_2, \\ \frac{1}{2}\alpha_2; 1, 1, -1) \\ = \frac{\Gamma(3/2 + \frac{1}{2}\alpha_1) \Gamma(\frac{1}{2} - \frac{1}{2}\alpha_1 - \frac{1}{2}\alpha_2)}{\Gamma(1 + \alpha_2) \Gamma(\frac{1}{2}\alpha_1 + \frac{1}{2}\beta_2)} \frac{\Gamma(\frac{1}{2} - \frac{1}{2}\alpha_2 - \frac{1}{2}\beta_2)}{\Gamma(3/2 - \frac{1}{2}\alpha_1)} \frac{\Gamma(\frac{1}{2} + \frac{1}{2}\alpha_1 + \frac{1}{2}\alpha_2)}{\Gamma(\frac{1}{2} + \frac{1}{2}\alpha_1 - \frac{1}{2}\alpha_2)} \times \\ \times \frac{\{ \Gamma(\frac{1}{2} + \frac{1}{2}\alpha_2 + \frac{1}{2}\beta_2) \}^2}{\Gamma(\frac{1}{2} - \frac{1}{2}\alpha_2 + \frac{1}{2}\beta_2) \Gamma(\frac{1}{2} + \frac{1}{2}\alpha_2 - \frac{1}{2}\beta_2)}.$$

The values of the functions  $F_N$  and  $F_R$  at the point  $(1, 1, -1)$  can similarly be obtained.

### 5. THE SUMS OF $F_F$ AND $F_D$

Writing [7, p. 312]

$$(5.1) \dots F_F(\alpha_1, \alpha_1, \alpha_1, \beta_1, \beta_2, \beta_1; \gamma_1, \gamma_2, \gamma_2; x, y, z) = \sum_{m=0}^{\infty} \frac{(\alpha_1, m)(\beta_1, m)}{(1, m)(\gamma_1, m)} F_1(\alpha_1 + m, \beta_2, \beta_1 + m; \gamma_2; y, z) x^m,$$

and using the relation (1.1) we get

$$(5.2) \dots F_F(\alpha_1, \alpha_1, \alpha_1, \beta_1, \beta_2, \beta_1; \gamma_1, \gamma_2, \gamma_2; x, 1, 1) = \frac{\Gamma(\gamma_2) \Gamma(\gamma_2 - \alpha_1 - \beta_1 - \beta_2)}{\Gamma(\gamma_2 - \alpha_1) \Gamma(\gamma_2 - \beta_1 - \beta_2)} \times \\ \times {}_4F_3 \left[ \begin{matrix} \alpha_1, \beta_1, 1 - \gamma_2 & \alpha_1, 1 - \gamma_2 + \beta_1 + \beta_2; \frac{1}{2}x \\ \gamma_1, \frac{1}{2} - \frac{1}{2}\gamma_2 + \frac{1}{2}\alpha_1 + \frac{1}{2}\beta_1 + \frac{1}{2}\beta_2, 1 - \frac{1}{2}\gamma_2 + \frac{1}{2}\alpha_1 + \frac{1}{2}\beta_1 + \frac{1}{2}\beta_2 \end{matrix} \right].$$

Now, applying (4.3) to sum the  ${}_4F_3$  in (5.2) we obtain

$$(5.3) \dots F_F(\alpha_1, \alpha_1, \alpha_1, \frac{1}{2}\alpha_1 + 1, \frac{1}{2}\alpha_1 - 3/2, \frac{1}{2}\alpha_1 + 1; \frac{1}{2}\alpha_1, 2/3\alpha_1 + 1/6, 2/3\alpha_1 + 1/6; -4, 1, 1) = - \frac{\{\Gamma(1/6 + 2/3\alpha_1)\}^2 \Gamma(2/3 + 2/3\alpha_1) \Gamma(2/3 - 4/3\alpha_1)}{\Gamma(1 + \alpha_1) \Gamma(1/3\alpha_1 - 1/6) \Gamma(2/3 - 1/3\alpha_1) \Gamma(1/6 - 1/3\alpha_1)}.$$

Also, an interchange in the denominator parameters of the  ${}_4F_3$  in (5.2) yields the result

$$(5.4) \dots F_F(\alpha_1, \alpha_1, \alpha_1, \frac{1}{2}\alpha_1 + 1, \frac{1}{2}\alpha_1 - \frac{1}{2}, \frac{1}{2}\alpha_1 + 1; \frac{1}{2}\alpha_1, 2/3\alpha_1 + 5/6, 2/3\alpha_1 + 5/6; -4, 1, 1) = - \frac{\{\Gamma(5/6 + 2/3\alpha_1)\}^2 \Gamma(1/3 + 2/3\alpha_1) \Gamma(1/3 - 4/3\alpha_1)}{\Gamma(1 + \alpha_1) \Gamma(1/3\alpha_1 + 1/6) \Gamma(1/3 - 1/3\alpha_1) \Gamma(5/6 - 1/3\alpha_1)}.$$

Again, following the notation of [4] we have

$$(5.5) \dots F_D(\alpha, \beta_1, \beta_2, \beta_3; \gamma; x, y, z)$$

$$= \sum_{p=0}^{\infty} \frac{(\alpha, p)(\beta_3, p)}{(1, p)(\gamma, p)} F_1(\alpha + p, \beta_1, \beta_2; \gamma + p; x, y) z^p,$$

and using the relation (1.1) we get

$$(5.6) \dots F_D(\alpha, \beta_1, \beta_2, \beta_3; \gamma; 1, 1, z) = \frac{\Gamma(\gamma) \Gamma(\gamma - \alpha - \beta_1 - \beta_2)}{\Gamma(\gamma - \alpha) \Gamma(\gamma - \beta_1 - \beta_2)} {}_2F_1(\alpha, \beta_3; \gamma - \beta_1 - \beta_2; z).$$

Applying (2.3) to sum the  ${}_2F_1$  in the above we obtain

$$(5.7) \dots F_D(\alpha, \beta_1, \beta_2, \beta_3; \gamma; 1, 1, -1) = \frac{\Gamma(\gamma) \Gamma(1 + \frac{1}{2}\alpha) \Gamma(1 - \beta_3)}{\Gamma(\gamma - \alpha) \Gamma(1 + \alpha) \Gamma(1 + \frac{1}{2}\alpha - \beta_3)}$$

provided that  $\gamma - \beta_1 - \beta_2 = 1 + \alpha - \beta_3$ .

If we use the relation (2.2) in (5.6) we get

$$(5.8) \dots F_D(\alpha, \beta_1, \beta_2, 1 - \alpha; \gamma; 1, 1, \frac{1}{2})$$

$$= \frac{\Gamma(\gamma) \Gamma(\lambda - \alpha) \Gamma(\frac{1}{2}\lambda) \Gamma(\frac{1}{2} + \frac{1}{2}\lambda)}{\Gamma(\lambda) \Gamma(\gamma - \alpha) \Gamma(\frac{1}{2}\lambda + \frac{1}{2}\alpha) \Gamma(\frac{1}{2} + \frac{1}{2}\lambda - \frac{1}{2}\alpha)},$$

where  $\lambda = \gamma - \beta_1 - \beta_2$ .

Lastly, using the relation [3, p. 104]

$$(5.9) \dots {}_2F_1(a, b; \frac{1}{2} + \frac{1}{2}\alpha + \frac{1}{2}b; \frac{1}{2}) = \frac{\Gamma(\frac{1}{2}) \Gamma(\frac{1}{2} + \frac{1}{2}\alpha + \frac{1}{2}b)}{\Gamma(\frac{1}{2} + \frac{1}{2}\alpha) \Gamma(\frac{1}{2} + \frac{1}{2}b)},$$

we obtain

$$(5.10) \dots F_D(\alpha, \beta_1, \beta_2, \beta_3; \gamma; 1, 1, \frac{1}{2})$$

$$= \frac{\Gamma(\frac{1}{2}) \Gamma(\gamma) \Gamma(\frac{1}{2} - \frac{1}{2}\alpha + \frac{1}{2}\beta_3)}{\Gamma(\gamma - \alpha) \Gamma(\frac{1}{2} + \frac{1}{2}\alpha) \Gamma(\frac{1}{2} + \frac{1}{2}\beta_3)},$$

this result being valid when  $\gamma - \beta_1 - \beta_2 = \frac{1}{2}(1 + \alpha + \beta_3)$ .

## 6. REGIONS OF CONVERGENCE

It may be mentioned that the series for Appell's function  $F_4$  is convergent when  $\sqrt{|x|} + \sqrt{|y|} < 1$ , but the function may be analytically continued over a wider field by a Barnes's integral of appropriate type.

For the hypergeometric functions of three variables considered in this paper the domains of convergence are given by

$$F_D : \quad r = s = t = 1$$

$$F_F : \quad rs = (1 - s)(s - t)$$

$$F_K : \quad (1 - r)(1 - s) = t$$

$$F_N : \quad (1 - r)s + (1 - s)t = 0$$

and

$$F_R : \quad s(1 - \sqrt{r})^2 + (1 - s)t = 0,$$

where  $|x| < r$ ,  $|y| < s$  and  $|z| < t$ , and it may be recalled that what is true with  $F_4$  is extensible suitably to these functions as well.

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# ON CHAINS OF MEIJER'S BESSEL TRANSFORM

By

P. N. KAIHIE

*Lecturer in Mathematics, Faculty of Engineering, University of Jodhpur, Jodhpur*

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## ABSTRACT

This paper deals with three lemmas involving Meijer's Bessel transform defined by

$$\phi(p) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} p \int_0^\infty (p)_{\nu}^{\frac{1}{2}} K_\nu(p t) f(t) dt.$$

The lemmas have been used to obtain certain other properties of the Meijer's Bessel transform involving chains. The results obtained are quite interesting and a chain involving Laplace transformation given earlier by Bose follows as a particular case of the theorem 1.

## 1. INTRODUCTION

The Laplace transform

$$\phi(p) = b \int_0^\infty e^{-pt} f(t) dt, \quad (1.1)$$

has been generalised by Meijer (3) in the form

$$\phi(p) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} p \int_0^\infty (pt)_{\nu}^{\frac{1}{2}} K_\nu(pt) f(t) dt. \quad (1.2)$$

When  $\nu = \pm \frac{1}{2}$ , (1.2) reduces to (1.1) by virtue of the well-known identity

$$K_{\pm \frac{1}{2}}(x) = \left(\frac{\pi}{2x}\right)^{\frac{1}{2}} e^{-x}.$$

We shall denote (1.1) and (1.2) symbolically as

$$\phi(p) \doteq f(t) \text{ and } \phi(p) \doteq \frac{k}{\nu} f(t)$$

respectively and  $\Delta(n; \alpha)$  stands for the set of parameters

$$\frac{\alpha}{n}, \frac{\alpha+1}{n}, \dots, \frac{\alpha+n-1}{n}.$$

2. The following results follow from Saxena's formulae [(4), p. 401, eq. 7,8]

$$\int_0^\infty t^{p+\frac{1}{2}} K_\nu(pt) G_{\gamma, \delta}^{\alpha, \beta} \left[ a t^{2n/s} \mid \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right] dt.$$

$$= \left( \frac{\pi}{2} \right)^{\frac{1}{2}} (2n)^{\beta} + \frac{1}{2} p^{-\rho - \frac{\delta}{2}} (2\pi)^{\frac{1}{2} - n + (1-s)(\alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2})}$$

$$s^{\sum b_i - \sum a_j + \frac{\gamma}{2} - \frac{\delta}{2} + 1} \times \\ G_{s\beta+2n, s\alpha}^{s\beta+2n, s\alpha} \left[ \frac{s(\gamma-\delta)}{a^s} \left( \frac{p}{2n} \right)^{2n} \middle| \begin{array}{l} \Delta(s; 1-b_1), \dots, \\ \Delta(n; \frac{3+2\rho \pm 2\nu}{4}), \\ \Delta(s; 1-b_\delta) \\ \Delta(s; 1-a_1), \dots, \Delta(s; 1-a_r) \end{array} \right] \quad (2.1)$$

for  $R \left\{ \min 2nb_h + \rho s \pm \nu s + \frac{3}{2}s \right\} > 0, h=1, 2, \dots, a; \alpha + \beta > \frac{1}{2}(\gamma + \delta);$

$$|\arg a| < \left( \alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2} \right) \pi; R(p) > 0.$$

$$G_{0, 2s}^{2s, 0} \left[ \left( \frac{x}{2s} \right)^{2s} \middle| \Delta(s; b_1), \Delta(s; b_2) \right] \\ = 2^{s-b_1-b_2-\frac{1}{2}} \pi^{s-\frac{1}{2}} s^{-b_1-b_2} x^{b_1+b_2-\frac{1}{2}} e^{-x}. \quad (2.2)$$

where  $s$  is a positive integer and  $b_1 - b_2 = \pm \frac{1}{2}$ .

3. *Lemma 1*: Verma [5], p. 201] has shown that

If

$$\phi(p) = \frac{k}{v_1} f_1(t)$$

and

$$p^{\frac{1}{2}} f_1 \left( \frac{1}{p} \right) = \frac{k}{v_2} f_2(t),$$

then

$$\phi(p) = 2^{-3/2} \pi^{-1} p \int_0^\infty t^{\frac{1}{2}} f_2(t) G_{0,4}^{4,0} \left[ \frac{p^2 t^2}{2^2} \middle| \frac{1 \pm 2\nu_1}{4}, \pm \frac{\nu_2}{2} \right] dt, \quad (3.1)$$

provided that  $R(p) > 0$ , the Meijer transforms of  $|f_1(t)|$  and  $|f_2(t)|$  exist and the integral is absolutely convergent.

*Lemma 2 :* If

$$p^{\rho} \phi_1(p^{\sigma}) = \frac{k}{\nu} t^{\lambda} f(t^{\mu}) \quad (3.2)$$

and

$$\phi_2(p) = \frac{k}{\nu} t^{-\rho-1} \phi_1(t^{-\sigma}), \quad (3.3)$$

then

$$p^{-3/2} \phi_2\left(\frac{p^2}{4}\right) = \frac{k}{2\nu} \left(\frac{\pi}{8}\right)^{\frac{1}{2}} t^{2\lambda-\frac{1}{2}} f(t^{2\mu}) \quad (3.4)$$

provided that  $R(p) > 0$ , the Meijer transforms of  $|t^{\lambda} f(t^{\mu})|$  and

$|t^{2\lambda-\frac{1}{2}} f(t^{2\mu})|$  exist and  $\rho, \sigma, \lambda, \mu$  are real quantities.

*Proof:* Applying Parseval-Goldstein theorem of the Meijer transform to (3.2) and [2] p. 146]

$$(2\pi p)^{\frac{1}{2}} K_{2\nu}(2a^{\frac{1}{2}} p^{\frac{1}{2}}) = \frac{k}{\nu} t^{-\frac{1}{2}} K_{\nu}\left(-\frac{a}{t}\right) \quad (3.5)$$

for  $R(a) > 0, R(p) > 0$ .

we have

$$\begin{aligned} & \int_0^\infty x^{\rho-3/2} K_{\nu}\left(-\frac{a}{x}\right) \phi_1(x^{\sigma}) dx \\ &= (2\pi)^{\frac{1}{2}} \int_0^\infty t^{\lambda-\frac{1}{2}} K_{2\nu}(2a^{\frac{1}{2}} t^{\frac{1}{2}}) f(t^{\mu}) dt. \end{aligned}$$

Replacing  $a$  by  $\frac{p^2}{4}$ ,  $x$  by  $\frac{1}{x}$ ,  $t$  by  $t^2$ , and interpreting the L.H.S. by

(3.3) we obtain (3.4).

*Lemma 3 :* If

$$p^{\rho} \phi_1(p^{\sigma}) = \frac{k}{\nu} t^{\lambda} f(t^{\mu})$$

and

$$\phi_2(p) = \frac{k}{\nu} t^{-\rho+1} \phi_1(t^{-\sigma}),$$

then

$$p^{\frac{1}{2}} \phi_2 \left( \frac{p^2}{4} \right) \frac{k}{2\nu} (2\pi)^{\frac{1}{2}} t^{2\lambda+3/2} f(t^{2\mu}), \quad (3.6)$$

provided that  $R(p) > 0$ , the Meijer transforms of  $|t^\lambda f(t^\mu)|$  and

$|t^{2\lambda+3/2} f(t^{2\mu})|$  exist and  $\rho, \sigma, \lambda, \mu$  are real quantities.

*Proof:* Proof of this lemma is similar to that of lemma 2, if we use the following result [(2), p. 146] instead of (3.5).

$$(2\pi)^{\frac{1}{2}} a^{-1} p^{3/2} K_{2\nu} (2a^{\frac{1}{2}} p^{\frac{1}{2}}) \frac{k}{\nu} t^{-5/2} K_\nu \left( \frac{a}{t} \right).$$

for  $R(a) > 0$ ,  $R(p) > 0$ .

#### 4. Theorem 1 : If

$$\phi(p) \frac{k}{\nu_1} f_1(t),$$

$$p^{\frac{1}{2}} f_1 \left( \frac{1}{p} \right) \frac{k}{\nu_2} f_2(t),$$

$$\frac{1}{2} \left( \frac{\pi}{p} \right)^{\frac{1}{2}} f_2 \left( \frac{1}{4p^2} \right) \frac{k}{\nu_3} f_3(t), \quad (4.1)$$

$$\frac{1}{2} \left( \frac{\pi}{p} \right)^{\frac{1}{2}} f_3 \left( \frac{1}{4p^2} \right) \frac{k}{\nu_4} f_4(t), \quad (4.2)$$

and

$$\frac{1}{2} \left( \frac{\pi}{p} \right)^{\frac{1}{2}} f_{n-1} \left( \frac{1}{4p^2} \right) \frac{k}{\nu_n} f_n(t),$$

then

$$\begin{aligned} \phi(p) = & 2^{-2\beta_n - \frac{n-1}{2}} \pi^{1-2} \frac{n-1}{p} \times \\ & \frac{n}{2} \left\{ 2^{2\rho_n - \beta_n + 3} (\beta_n)^{\rho_n + \frac{1}{2}} \right\} \int_0^\infty t^{\alpha_n} f_n \left( \frac{t^2}{4} \right) \times \\ & [46] \end{aligned}$$

$$G_{0, 2\alpha_n}^{2\alpha_n, 0} \left[ \frac{p^2 t^{2\alpha_n}}{2^n \prod_{k=1}^n \left\{ \alpha_k \alpha_n 2^{2\alpha_n} \right\}} \right] dt$$

$$\left[ \frac{1 \pm 2\nu_1}{4}, \pm \frac{\nu_2}{2}, \Delta \left( 2; \frac{-1 \pm \nu_3}{2} \right), \dots, \Delta \left( \frac{n-2}{2}; \frac{-2+1 \pm \nu_n}{2} \right) \right] dt.$$

provided that  $R(p) > 0$ , the Meijer transforms of  $|f_i(t)|$  for  $i = 2, 3, \dots, n$  all exist, the integrals involved are absolutely convergent. Here

$$\alpha_n = 2^{n-1}, \beta_n = 2^{n-2}, \rho_n = -\frac{1}{2} - 2^{n-2} \text{ and } \prod_{k=1}^n$$

indicates the product of the factors within bracket for  $n = 2$  to any integral value of  $n$ .

*Proof:*—Substituting the value of  $f_2(t)$  from (4.1) in (3.1), interchanging the order of integration and integrating the later integral, it is found that

$$\phi(p) = 2^{-8} \pi^{-3} p \int_0^\infty t^{3/2} f_2(t) \times$$

$$G_{0, 8}^{8, 0} \left[ \frac{p^{2/4}}{2^{16}} \left| \frac{1 \pm 2\nu_1}{4}, \pm \frac{\nu_2}{2}, \Delta \left( 2; \frac{-1 \pm \nu_3}{2} \right) \right] dt.$$

Repeating this process successively with the correspondences (4.2), (4.3) ...

and replacing  $t$  by  $\frac{t^2}{4}$  in the end, we arrive at the result.

*Corollary:* Taking  $\nu_1 = \nu_2 = \dots = \nu_n = \pm \frac{1}{2}$  and using (2.2) we obtain the following result involving Laplace transformation given earlier by Bose [1], p. 3].

If

$$\phi(p) \doteq f_1(t),$$

$$p^{\frac{1}{2}} f_1(p) \doteq f_2(t),$$

$$\frac{1}{2} \left( \frac{\pi}{p} \right)^{\frac{1}{2}} f_2 \left( \frac{1}{4p^2} \right) \doteq f_3(t),$$

$$\frac{1}{2} \left( -\frac{\pi}{p} \right)^{\frac{1}{2}} f_3 \left( -\frac{1}{4p^2} \right) \doteq f_3(t),$$

and

$$\frac{1}{2} \left( -\frac{\pi}{p} \right)^{\frac{1}{2}} f_{n-1} \left( \frac{1}{4p^2} \right) \doteq f_n(t),$$

then

$$\phi \left( \begin{array}{c} p^{2n}-1 \\ \end{array} \right) \doteq \frac{\pi^{\frac{1}{2}}}{2} \cdot t f_n \left( \begin{array}{c} t^2 \\ 4 \end{array} \right),$$

provided that  $R(p) > 0$ , the Laplace transforms of  $|f_i(t)|$  and  $|t f_i\left(\frac{t^2}{4}\right)|$  for  $i = 2, 3, \dots, n$  all exist.

### 5. Theorem 2: If

$$p^\rho \phi_1(p^\sigma) = \frac{k}{v} t^\lambda f(t^\mu),$$

$$\phi_2(p) = \frac{k}{v} t^{-\rho-1} \phi_1(t^{-\sigma}),$$

$$p^{-1} \phi_3(p) \frac{k}{2v} \left( \frac{8}{\pi} \right)^{\frac{1}{2}} t^{5/2} \phi_2 \left( -\frac{1}{4t^2} \right), \quad (5.1)$$

$$p^{-1} \phi_4(p) \frac{k}{2^{2p}} \left( \frac{8}{\pi} \right)^{\frac{1}{2}} t^{5/2} \phi_8 \left( -\frac{1}{4t^2} \right), \quad (5.2)$$

and

$$P^{-1} \phi_n(P) \frac{k}{2^{n-2}\nu} \left( -\frac{8}{\pi} \right)^{\frac{1}{2}} t^{5/2} \phi_{n-1} \left( \frac{1}{4t^2} \right),$$

then

$$p^{-3/2} \phi_n \left( \frac{p^2}{4} \right) = \frac{k}{2^{n-1} \nu} \left( \frac{\pi}{8} \right)^{\frac{1}{2}} t^{2^{\frac{n-1}{2}} \lambda - 3/2 + 2^{\frac{n-1}{2}}} f(t^{2^{\frac{n-1}{2}} \mu})$$

provided that  $R(p) > 0$ , the Meijer transforms of  $| t^\lambda f(t^\mu) |$

$$\text{and } \left| t^{2^{\frac{i-1}{2}} \lambda - \frac{3}{2} + 2^{\frac{i-2}{2}}} f(t^{2^{\frac{i-1}{2}} \mu}) \right| \text{ for } i = 2, 3, \dots n$$

all exist and  $\rho, \sigma, \lambda, \mu$  are real quantities.

*Proof :* Substituting the value of  $\phi_2 \left( \frac{1}{4t^2} \right)$  from (3.4) changing the order of integration and evaluating the later integral we obtain.

$$p^{-1} \phi_3(p) = 2 p^{\frac{1}{2}} \int_0^\infty t^{2\lambda} f(t^{2\mu}) k_{4\nu}(2\sqrt{pt}) dt.$$

Replacing  $p$  by  $\frac{p^2}{4}$  and  $t$  by  $t^2$  we obtain

$$p^{-3/2} \phi_3 \left( \frac{p^2}{4} \right) = \frac{k}{4\nu} \left( \frac{\pi}{8} \right)^{\frac{1}{2}} t^{4\lambda + \frac{1}{2}} f(t^{4\mu}).$$

By repeating this process successively with the relations (5.2), (5.3), ... we arrive at the result.

By adopting a similar procedure and using (3.6) instead of (3.4) we find

*Theorem 3 :* If

$$p^\rho \phi_1(p^\sigma) = \frac{k}{\nu} t^\lambda f(t^\mu),$$

$$\phi_2(p) = \frac{k}{\nu} t^{-\rho+1} \phi_1(t^{-\sigma}),$$

$$p \phi_3(p) = \frac{k}{2\nu} (2\pi)^{-\frac{1}{2}} t^{-3/2} \phi_2 \left( \frac{1}{4t^2} \right),$$

$$p \phi_4(p) = \frac{k}{2^2 \nu} (2\pi)^{-\frac{1}{2}} t^{-3/2} \phi_3 \left( \frac{1}{4t^2} \right),$$

$$\begin{array}{ccccccccccccccccccccccccc} \cdot & \cdot \\ , & , \end{array}$$

and

$$p \phi_n(p) \cdot \frac{k}{2^{\frac{n-2v}{2}}} (2\pi)^{-\frac{1}{2}} t^{-3/2} \phi_{n-1} \left( -\frac{1}{4t^2} \right),$$

then

$$p^{\frac{1}{2}} \phi_n \left( -\frac{p^2}{4} \right) \frac{k}{2^{\frac{n-2v}{2}}} (2\pi)^{\frac{1}{2}} t^{\frac{1}{2}} + 2^{n-1} \lambda + 2^{n-2} f \left( t^2 \begin{smallmatrix} n-1 \\ \mu \end{smallmatrix} \right).$$

provided that  $R(p) > 0$ , the Meijer transforms of  $| t^\lambda f(t^\mu) |$ ,

$$\left| t^{\frac{1}{2}+2^{-i-1}\lambda+2^{-i-2}} f \left( t^2 \begin{smallmatrix} i-1 \\ \mu \end{smallmatrix} \right) \right|, \text{ for } i = 2, 3, \dots, n \text{ all exist and } \rho, \sigma, \lambda, \mu$$

are real quantities.

6. To verify the theorem 2, for  $n = 3$ , we take  $\rho = 0, \sigma = 1, \lambda = 0, \mu = 1$  and let

$$f(t) = t^\rho G_{\gamma, \delta}^{\alpha, \beta} \left[ a t^2 \left| \begin{smallmatrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{smallmatrix} \right. \right],$$

then from (2.1) we have

$$\phi_1(p) = 2^\rho \pi^{-\frac{1}{2}} p^{-\rho} G_{\delta, \gamma+2}^{\beta+2, \alpha} \left[ \frac{p^2}{4a} \left| \begin{smallmatrix} 1-b_1, \dots, 1-b_\delta \\ \frac{3+2\rho \pm 2v}{4}, 1-a_1, \dots, 1-a_\gamma \end{smallmatrix} \right. \right]$$

provided that  $R \{ \min 2b_h + \rho \pm v + 3/2 \} > 0, h = 1, 2, \dots, \alpha ; \alpha + \beta > \frac{1}{2}(\gamma + \delta)$ ;

$$|\arg a| < \left( \alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2} \right) \pi, R(p) > 0.$$

Hence

$$t^{-1} \phi_1 \left( -\frac{1}{t} \right) = 2^\rho \pi^{-\frac{1}{2}} p^{\rho-1}$$

$$G_{\delta, \gamma+2}^{\beta+2, \alpha} \left[ \frac{1}{4at^2} \left| \begin{smallmatrix} 1-b_1, \dots, 1-b_\delta \\ \frac{3+2\rho \pm 2v}{4}, 1-a_1, \dots, 1-a_\delta \end{smallmatrix} \right. \right]$$

therefore

$$\phi_2(p) = 2^{\frac{2\rho-1}{\pi}} \pi^{-1} p^{-\rho+1}$$

$$G_{\delta, \gamma+4}^{\beta+4, \alpha} \left[ \frac{t^2}{4^2 a} \mid \begin{array}{c} 1-b_1, \dots, 1-b_\delta \\ \frac{1+2\rho \pm 2\nu}{4}, \frac{3+2\rho \pm 2\nu}{4}, 1-a_1, \dots, 1-a_\gamma \end{array} \right]$$

provided that  $R \{ \min 2b_h + \rho \pm \nu + \frac{1}{2} \} > 0, h = 1, 2, \dots, \alpha; \alpha + \beta + 1 > \frac{1}{2}(\gamma + \delta);$

$$|\arg a| < \left( \alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2} + 1 \right) \pi, R(p) > 0.$$

Hence

$$\left( \frac{8}{\pi} \right)^{\frac{1}{2}} t^{5/2} \phi_2 \left( \frac{1}{4t^2} \right) = 2^{\frac{4\rho-3/2}{\pi}} t^{-3/2} t^{2\rho+\frac{1}{2}} \times$$

$$G_{\delta, \gamma+4}^{\beta+4, \alpha} \left[ \frac{t^4}{4^4 a} \mid \begin{array}{c} 1-b_1, \dots, 1-b_\delta \\ \frac{1+2\rho \pm 2\nu}{4}, \frac{3+2\rho \pm 2\nu}{4}, 1-a_1, \dots, 1-a_\gamma \end{array} \right]$$

therefore

$$p^{-1} \phi_3(p) = 2^{3\rho-1} \pi^{-3} p^{-2\rho-\frac{1}{2}} \times$$

$$G_{\delta, \gamma+8}^{\beta+8, \alpha} \left[ \frac{p^4}{4^8 a} \mid \begin{array}{c} 1-b_1, \dots, 1-b_\delta \\ \frac{1+\rho \pm \nu}{2}, \frac{2+\rho \pm \nu}{2}, \frac{1+2\rho \pm 4\nu}{4}, \frac{3+2\rho \pm 4\nu}{4}, 1-a_1, \dots, 1-a_\gamma \end{array} \right]$$

provided that  $R \{ \min 2b_h + \rho \pm \nu + 1 \} > 0, h = 1, 2, \dots, \alpha, \alpha + \beta + 2 > \frac{1}{2}(\gamma + \delta);$

$$|\arg a| < \left( \alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2} + 2 \right) \pi, R(p) > 0.$$

Hence the theorem gives

$$p^{-4\rho-\frac{1}{2}} G_{\delta, \gamma+8}^{\beta+8, \alpha} \left[ \frac{p^8}{8^8 a} \mid \begin{array}{c} 1-b_1, \dots, 1-b_\delta \\ \frac{1+\rho \pm \nu}{2}, \frac{2+\rho \pm \nu}{2}, \frac{1+2\rho \pm 4\nu}{4}, \\ \frac{3+2\rho \pm 4\nu}{4}, 1-a_1, \dots, 1-a_\gamma \end{array} \right]$$

$$\frac{k}{4\nu} \pi^{7/2 \cdot \frac{1}{2} - 12\rho} t^{4\rho + \frac{1}{2}} G_{\gamma, \delta}^{\alpha, \beta} \left\{ at^8 \middle| \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right\}$$

for  $R \{ \min 4b_h + 2\rho \pm 2\nu + 1 \} > 0, h=1, 2, \dots, \alpha ; \alpha + \beta > \frac{1}{2}(\gamma + \delta)$ ;

$$|\arg a| < \left( \alpha + \beta - \frac{\gamma}{2} - \frac{\delta}{2} \right) \pi, R(p) > 0,$$

which is a particular case of (2.1) and hence the theorem is verified.

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# ON LINEAR ASYMPTOTES

By

R. C. KHARE

*Department of Mathematics, University of Allahabad, Allahabad*

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## SUMMARY

It has been established that the various definitions of a Linear Asymptote are not completely consistent and that the treatment of the case of failure viz., the case of parallel asymptotes is faulty. The case of real failure is distinguished from that of an apparent one. A modification is suggested to remove the difficulty.

§ 1.

A Linear Asymptote has been defined in the following three ways—

I—If a straight line cuts a curve in two points at an infinite distance from the origin and yet is not itself wholly at infinity, it is called an asymptote to the curve.<sup>1</sup>

II—An asymptote is the limiting position of the tangent to a curve when the point of contact moves away along the curve to an infinite distance from the origin, while the tangent itself does not ultimately lie wholly at infinity.<sup>2</sup>

III—An asymptote is a straight line whose distance from a point on the curve diminishes indefinitely as the point moves away along the curve to an infinite distance from the origin.<sup>3</sup>

Arranging the equation of any curve of the  $n$ th degree in homogeneous sets of terms we can put it in the form

$$x^n \phi_n \left( \frac{y}{x} \right) + x^{n-1} \phi_{n-1} \left( \frac{y}{x} \right) + \dots = 0 \quad \dots (1)$$

If  $y = \mu x + \beta$  be an asymptote,  $\mu$  and  $\beta$  are given by the equations

$$\phi_n(\mu) = 0 \quad \dots (2)$$

$$\beta \phi'_n(\mu) + \phi_{n-1}(\mu) = 0 \quad \dots (3)$$

Equations (2) and (3) have been obtained by substituting  $y = \mu x + \beta$  in (1) and equating to zero the coefficients of two highest powers of  $x$  in the resulting equation. Thus two of the roots become infinite and we get the eqn. to an asymptote according to the definition 1.

Edwards has shown that the same two equations are obtained for determining  $\mu$  and  $\beta$  if the other two definitions are followed. Thus he has tried to establish the consistency of all the definitions.<sup>4</sup>

But on close examination it is found that the consistency has been established only partially.

In Art 244, III of the treatise referred we have that if  $\phi_n(\mu) = 0$  have a pair of equal roots each equal to  $\mu_1$ , then  $\phi'_{n-1}(\mu_1) = 0$  and if further  $\mu_1$  be also a root of  $\phi_{n-1}(\mu) = 0$ , the value of  $\beta$  cannot be determined from the eqn.

$$\beta \phi'_n(\mu) + \phi_{n-1}(\mu) = 0$$

By equating to zero the coeff. of  $x^{n-2}$  in the eqn (1), we get

$$\frac{\beta^2}{2} \phi_n''(\mu) + \beta \phi_{n-1}'(\mu) + \phi_{n-2}(\mu) = 0 \quad \dots (4)$$

from which two values of  $\beta$ , real or imaginary may be deduced. Thus we get two parallel straight lines  $y = \mu_1 x + \beta_1$ ;

$$y = \mu_1 x + \beta_2.$$

each of which cuts the curve in three points at an infinite distance from the origin.

Now Edwards does not proceed to consider this case of apparent failure while adopting the other two definitions of an asymptote. Hence the consistency of the three definitions has been established only partially. The eqn. determining  $\beta$  in this case, has not been deduced.

### § 2.

Following Todhunter<sup>5</sup> (cf Diff. Cal. by Todhunter), some authors have adopted the second definition of an asymptote.

If  $y = mx + c$  be an asymptote, the equations for  $m$  and  $c$  are

$$\phi_n(m) = 0 \quad \dots (5)$$

$$c \phi_n'(m) + \phi_{n-1}(m) = 0 \quad \dots (6)$$

In the case when  $\phi_n'(m_1) = 0$ ;  $\phi_{n-1}(m_1) = 0$  the eqn. (6) fails to give a unique value of  $c$ . Then the authors remark that to determine  $c$ , we have now the eqn.

$$\frac{1}{2} c^2 \phi_n''(m) + c \phi_{n-1}'(m) + \phi_{n-2}(m) = 0 \quad \dots (7)$$

which follows from

$\phi_n\left(\frac{y}{x}\right) + \frac{1}{x} \phi_{n-1}\left(\frac{y}{x}\right) + \frac{1}{x^2} \phi_{n-2}\left(\frac{y}{x}\right) + \dots = 0$  on differentiating twice; multiplying out by a suitable power of  $x$  and taking limits.

On actually working out as stated above, the eqn. (7) is not deducible. And there is reason to believe that this eqn cannot be deduced on the assumption of the second definition of an asymptote. Todhunter (cf Art. 275 Diff. Calculus), on the other hand deduces an eqn. analogous to the eqn. (7) above by a procedure which in essence is the same as under definition I.

### § 3.

From the procedure of Edwards, it is obvious, that in case two-point intersection at infinity fails to give a unique value of  $\beta$ , he proceeds to consider the 3-point intersection at infinity. If this also fails, which will happen if  $\phi_n(m) = 0$  has 3 equal roots each equal to  $\mu_1$  and  $\phi_{n-1}'(\mu_1) = 0$  and  $\phi_{n-2}(\mu_1) = 0$ , then we can proceed to consider the 4 point intersection at infinity and can equate to zero the coeff. of  $x^{n-3}$  in the eqn. of the curve.

But adopting the second definition of an asymptote, which accepts the tangent concept, it is clear that we cannot start with a linear tangent which has a three point contact with the curve. And hence there is no possibility of obtaining an eqn. for  $\beta$  in the case of failure.

#### § 4.

To obviate all these difficulties, let us consider the eqns. determining  $\mu$  and  $\beta$  viz. eqns. (2) and (3).

If we accept the tangent concept of an asymptote, we must recognize that as the point of contact moves to infinity  $\mu$  must be regarded as tending to the values  $\mu_1, \mu_2$  etc. which are the roots of equation (1). Hence

$$\beta = \left[ \frac{-\phi'_{n-1}(\mu)}{\phi'_n(\mu)} \right]$$

*Lt*  $\mu \rightarrow \mu_1, \mu_2$  etc.

If  $\mu = \mu_1$  be a common factor of  $\phi'_n(\mu)$  and  $\phi'_{n-1}(\mu)$ , we get for  $\beta$  an *indeterminate form* which is easily evaluated.

Thus the failure to obtain a unique value of  $\beta$  was only superficial. Hence there is no need to proceed to a three point contact or a three point intersection at infinity.

#### § 5.

We consider the case of failure more closely. We have just concluded that if eqn. (1) has a repeated root  $\mu_1$ , and if further  $\phi'_{n-1}(\mu_1) = 0$ , then  $\beta$  can be determined as

$$\beta = \left[ \frac{-\phi'_{n-1}(\mu)}{\phi'_{n-1}(\mu)} \right],$$

*Lt*  $\mu \rightarrow \mu_1$

the undetermined form being evaluated. In this case, therefore, the failure was only apparent.

If on the other hand  $\phi'_{n-1}(\mu)$  is actually absent and  $\phi'_{n-1}(\mu_1) = 0$ , then the equation for  $\beta$  is  $\beta \phi'_{n-1}(\mu_1) = 0$ . Since  $\phi'_{n-1}(\mu_1) = 0$ ,  $\beta$  can have any arbitrary value. In this case the failure is real.

We consider the following examples.

$$x^3 + x^2y - xy^2 - y^3 + x^2 - y^2 = 2 \quad \dots (8)$$

$$y^3 + x^2y + 2xy^2 - y + 1 = 0 \quad \dots (9)$$

Eqn. (8) is of the form  $x^3 \phi_3 + x^2 \phi_2 + \phi_0 = 0$

Eqn. (9) . . .  $x^3 \phi_3 + x \phi_2 + \phi_0 = 0$

For eqn. (8) we have

$$\phi_3 = 1 + \mu - \mu^2 - \mu^3$$

$$= (1 - \mu)(1 + \mu)^2$$

$$\phi_2 = (1 - \mu^2)$$

Therefore for the repeated root  $\mu = -1$ , we have

$$\begin{aligned}\beta &= Lt \left[ - \frac{1 - \mu^2}{-(1+\mu)^2 + 2(1-\mu)(1+\mu)} \right] \\ \mu &\rightarrow -1 \\ &= -\frac{1}{2}\end{aligned}$$

Hence the asymptotes are

$$y = x, y = -x - \frac{1}{2}; y = -x + \frac{1}{2}.$$

The two parallel asymptotes are coincident.

For eqn. (9) we have

$$\begin{aligned}\phi_3(\mu) &= \mu^3 + \mu + 2\mu^2 \\ &= \mu(1+\mu)^2\end{aligned}$$

$\phi_2(\mu)$  is absent

$$\phi'_3(\mu) = 0 \text{ for } \mu = -1, \text{(the repeated root)}$$

$$\phi''_3(\mu) = 1 \text{ for } \mu = 0.$$

Therefore for  $\mu = 0, \beta = 0$ ;

for  $\mu = -1, \beta$  can have any arbitrary value. One asymptote is  $y = 0$ . The other asymptotes are indeterminate. It is this case, therefore, which presents real difficulty.

It is clear from our discussion that the Tangent concept of an asymptote does not provide us with any other equation to determine  $\beta$ . But the first definition can still help us out of the difficulty. We get the eqn. (4) for  $\beta$  by equating to zero the coeff. of  $x^{n-2}$  in the equation.

We thus differentiate the case of real failure to determine  $\beta$  from the one of apparent failure.

## § 6.

### CONCLUSION

The three definitions of a Linear Asymptote are only partially consistent. The so-called case of failure must be studied in two parts viz., the case of apparent failure and the case of real failure.

The case of apparent failure can be tackled without bringing in the three-pt intersection of the asymptote with the curve; whereas the case of real failure can be dealt with completely only according to the first definition. The Tangent-concept does not lead us further.

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# ON THE ROLE OF OPERATORS AS OBSERVABLES IN QUANTUM THEORY—I

By

R. L. DASVARMA

*Department of Mathematics, L. S. College, Muzaffarpur*

[ Received on 7th October, 1964 ]

## ABSTRACT

In this paper, the axioms on observables, their measured values and their expected means in a sequence of measurements have been deduced from an axiom on the correspondence between states an Hilbert vectors and from the interpretation of the inner products of these vectors in terms of the probabilities of transition between different states.

Only the case of non-degenerate states corresponding to discrete measurable values of observables has been considered by making use of the statistical operator of von Neumann.

1. In an axiomatic foundation of quantum theory a complete system of axioms are :<sup>1</sup>

- (i) To every state of a physical system there corresponds a vector in a Hilbert space.
- (ii) To every observable associated with the system there corresponds a linear Hermitian operator in this Hilbert space.
- (iii) The only possible values which a measurement of an observable A yields are the eigenvalues  $\alpha_i$  of the equation

$$(1 \cdot 1) \quad Aa_i = \alpha_i a_i$$

where A is the operator corresponding to the observable A and  $a_i$  are the vectors representing the different states in which A has the values  $\alpha_i$ .

(iv) When a system is in the state represented by the vector  $u$ , the expected mean of a sequence of measurements on the observable whose operator is A, is given by

$$(1 \cdot 2) \quad \overline{\alpha} = (u, Au),$$

where the right hand side is the inner product of  $u$  and  $Au$ .

The intuitive meaning attached to the state vector is that the inner product  $(u, v)$  of two vectors  $u$  and  $v$ , representing two states defines the probability of the system making a transition from the state  $u$  to the state  $v$  as a result of a measurement.

$$(1 \cdot 3) \quad |(u, v)|^2 = Pr. (u \rightarrow v) = Pr. (v \rightarrow u).$$

The four axioms together with (1.3) are sufficient to evolve the whole of quantum statics. For quantum dynamics, however, a further axiom has to be added to prescribe the change of states in time.

Sometimes the probabilistic interpretation is taken as an axiom in place of (iv).

2. It can be shown that only the axiom (i) together with the probabilistic interpretation expressed by (1·3) is sufficient for deducing the axioms (ii), (iii) and (iv). We shall restrict ourselves here to only observables which can have discrete values as results of measurement.

Let the states characteristic of a given observable A (*i.e.*, corresponding to well-defined values  $a_i$  of A) be represented by vectors  $a_i$ ,  $i = 1, 2, \dots$ , in a Hilbert space. Since  $\text{Pr.}(a_i \rightarrow a_i) = 1$ ,  $\text{Pr.}(a_i \rightarrow a_j) = 0$ ,  $i \neq j$ , it follows from (1·3) that the set  $\{a_i\}$  of Hilbert vectors form an orthonormal set. Since there is no state of the system, which is not characteristic of A, such that the probability of transition of the system from this state to each characteristic state of A is zero, there is no vector  $u$ , not belonging to the set  $\{a_i\}$ , such that  $(u, a_i) = 0$ , for every  $i$ . Therefore the orthonormal set  $\{a_i\}$  is complete and forms a basis in the Hilbert space. Therefore, the vectors representing the characteristic states of an observables form a complete orthonormal set.

Any vector  $u$ , representing an arbitrary state, is a linear combination of the orthonormal set  $\{a_i\}$ , representing the characteristic states of the observable A :

$$(2·1) \quad u = \sum_i (u, a_i) a_i, \quad \text{Pr.}(u \rightarrow a_i) = |(u, a_i)|^2,$$

$$(2·2) \quad \|u\| = \sqrt{\sum_i |(u, a_i)|^2} = \sqrt{\sum_i \text{Pr.}(u \rightarrow a_i)} = 1,$$

Since when the system is in the state  $u$ , an A-measurement is sure to result in one of the values  $a_i$  of A, *i.e.*, the system is sure to make a transition to one of the states  $a_i$ , characteristic of A. Hence the vectors representing states will usually be taken to be of unit norm.

3. Putting  $(u, a_i) = u_i$ , we next form von Neumann's<sup>2</sup> statistical operator  $U$ , whose matrix of representation with respect to  $\{a_i\}$  is given by

$$(3·1) \quad U_{ij} = u_i u_j^*.$$

From its definition it is evident that  $U$  is Hermitian. That it is idempotent can be seen from the fact that

$$(U^2)_{ij} = \sum_k U_{ik} U_{kj} = \sum_k u_i u_k^* u_k u_j^* = u_i u_j^* = U_{ij}, \text{ from (2·2), so that}$$

$$(3·2) \quad U^2 = U.$$

Thus  $U$  is a projection operator. It projects any arbitrary vector  $v$  into vector which is a multiple of  $u$ ,

$$(3·3) \quad Uv = (v, u) u.$$

$U$  is the statistical operator for the state  $u$ .

The statistical operator for the state  $a_m$  is given by

$$(3\cdot 4) \quad (E_m)_{ij} = \delta_{mi} \delta_{mj} = \begin{cases} 1, & i = j = m \\ 0, & \text{otherwise} \end{cases}$$

Thus, its matrix is an elementary matrix in the representation with  $\{a_i\}$  as basis, with one element in the  $m^{\text{th}}$  diagonal position equal to unity and all others zero. Hence  $E_m$  is an elementary projection.

It is clear that the set of elementary projections  $\{E_m\}$  project a vector into mutually orthogonal vectors  $a_m$ . Therefore  $\{E_m\}$  is a set of mutually orthogonal elementary projections:

$$(3\cdot 5) \quad E_m E_n = \delta_{mn} E_m.$$

$E = \sum_m E_m$  is also a projection and for any vector  $u$ , we have

$$Eu = (\sum_m E_m) u = \sum_m (u, a_i) a_i = u$$

so that

$$(3\cdot 6) \quad E = \sum_m E_m = 1.$$

A set of projections  $\{E_m\}$  with properties (3·5) and (3·6) is said to be a resolution of the identity.

4. Form an operator A by setting

$$(4\cdot 1) \quad A = \sum_m a_m E_m.$$

A is evidently Hermitian since every  $E_m$  is so. Further,

$$(4\cdot 2) \quad Aa_m = \sum_n a_n E_n a_m = \sum_n a_n \delta_{nm} a_m = a_m a_m.$$

But (4·2) shows that  $a_m$  are the eigenvectors of A belonging to the eigenvalues  $a_m$ .

Since corresponding to every observable A there exists a complete orthonormal set of vectors representing the characteristic states of the observable A with values  $a_m$ , and since corresponding to every complete orthonormal set of vectors there is a resolution of the identity, we can correspond every observable by a Hermitian operator in Hilbert space. This operator represents the observable in the following sense: The eigenvalues of the operator are the different values, the observable will have on measurement and its eigenvector represent the different states characteristic of this observable.

Thus the axioms (ii) and (iii) are established.

5. In order to deduce the axiom (iv), we first note that with respect to the orthonormal set  $\{a_i\}$ , the operator A has a diagonal representation.

$$(5\cdot 1) \quad A_{ij} = (a_i, Aa_j) = (a_i, a_j, a_j) = a_i \delta_{ij}$$

The mean value  $\bar{\alpha}$  of A in a sequence of measurements, when the system is in the state  $u$ , is

$$(5.2) \quad \bar{\alpha} = \sum_i |u_i|^2 \alpha_i = \sum_i u_i u_i^* \alpha_i = \sum_i \sum_j u_i u_j^* \alpha_j \delta_{ij} = \sum_i \sum_j U_{ij} A_{ij}$$

$$= \sum_i (\text{UA})_{ii} = t_r(\text{UA}).$$

But

$$t_r(\text{UA}) = \sum_i (\text{UA})_{ii} = \sum_i (a_i, \text{UA } a_i) = \sum_i (a_i, \text{U}^2 \text{A } a_i)$$

$$= \sum_i (\text{U}a_i, \text{UA } a_i) \quad (\text{since U is a projection})$$

$$= \sum_i u_i^* (\text{A } u)_i = (u, \text{A } u).$$

Hence

$$(5.3) \quad \bar{\alpha} = (u, \text{A } u).$$

This establishes axiom (iv).

We have assumed here that the each characteristic state of the observable A correspond to different measurable values of A but the method of proof can be extended to the case where corresponding to a particular value of A there are several states characteristic of this value of A.

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# ASYMPTOTIC STABILITY OF A NON-LINEAR DIFFERENTIAL SYSTEM

By

D. RAMAKRISHNA RAO

Lecturer in Mathematics, Department of Technical Education, Secunderabad (A. P.)

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## ABSTRACT

In this paper the author has studied the stability behavior of the Differential system

$$\frac{dx}{dt} = Ax + f(t, x)$$

under the non-linearity condition

$$\frac{|f(t, x)|}{|x|} \leq M \cdot e^{\alpha t} \cdot |x|^{\beta}.$$

A lemma which has been proved elsewhere, is used here to prove the theorem.

Considerable research has been done on the problem of studying the stability behavior of the solutions of a differential system

$$(1) \quad \frac{dx}{dt} = Ax + f(t, x)$$

under various conditions upon the non-linear term  $f(t, x)$ . In this paper we study the behavior of the solutions under a powerful restriction upon the non-linear term. We make use of the following lemma 1 in the proof of our Theorem.

*Lemma 1:*—Let  $\theta, \psi, x$  be real valued continuous or piecewise continuous functions in the interval  $I : a \leq t \leq b$ .

Let  $x(t) > 0$  on I and suppose for  $t \in I$  that

$$\theta(t) \leq \psi(t) + \int_a^t x(s) \cdot \theta(s) ds.$$

then on I

$$\theta(t) \leq \psi(t) + \int_a^t x(s) \psi(s) \exp \left( \int_s^t x(u) du \right) ds$$

This Lemma has been proved by the author in (2).

**Lemma 2:**—In Lemma I, if

$$\theta(t) \geq \psi(t) - \int_a^t \chi(s) \theta(s) ds$$

Then

$$\theta(t) \geq \psi(t) - \int_a^t \chi(s) \psi(s) \exp\left(\int_s^t \chi(u) du\right) ds$$

*Proof Lemma 2:*—The proof is quite similar to Lemma 1

**Theorem :**— If

$$(2) \quad (a) \text{ for } |x| \leq \delta \text{ with } \delta > 0$$

$$\frac{|f(t, x)|}{|x|} \leq M. e^{\alpha t}. |x|^{\beta}.$$

where in,  $\alpha$  and  $\beta$  are positive constants for all  $t \geq 0$

(b)  $A$  is a constant matrix with the characteristic roots all having negative real parts so that

$$|\gamma(t)| \leq k. e^{-\sigma t}$$

where  $\gamma(t)$  is the principal matrix solution of the linear system

$$\frac{dx}{dt} = Ax$$

$K$ . and  $\sigma$  are positive constants then if  $\alpha < M\sigma$ , the trivial solution of (1) is asymptotically stable.

*Proof of theorem:*—The solution  $\theta$  of (1) with  $|\theta(0)|$  small for  $t \geq 0$  can be written as

$$(3) \quad \theta(t) = e^{tA} \theta(0) + \int_0^t e^{(t-s)A} f(s, \theta(s)) ds$$

using 2 (b) we obtain

$$(4) \quad \theta(t) = k. |\theta(0)| e^{-\sigma t} + k \int_0^t e^{-(t-s)\sigma} |f(s, \theta(s))| ds$$

which can be written as

$$(5) \quad e^{\sigma t} |\theta(t)| \leq k |\theta(0)| + k \int_0^t |f(s, \theta(s))| e^{\sigma s} ds.$$

so long as  $|\theta(t)| \leq \delta$ , using the hypothesis 2 (a) we obtain

$$(6) \quad e^{\sigma t} |\theta(t)| \leq k |\theta(0)| + K \cdot m. \int_0^t e^{\alpha s} \cdot |\theta(s)|^\beta \cdot e^{\sigma s} |\theta(s)| ds$$

Applying Lemma 1 we have

$$(7) \quad e^{\sigma t} |\theta(t)| \leq k |\theta(0)| \exp \left[ K \cdot m. \int_0^t |\theta(s)|^\beta e^{\alpha s} ds \right]$$

Hence

$$\theta(t) \leq . |\theta(0)| \exp \left[ K^2 \cdot m. \int_0^t |\phi(s)|^\beta ds - (\sigma\beta - \alpha) t \right]$$

where

$$\phi(t) = \frac{\theta(t) e^{\sigma t}}{K}.$$

Let

$$|\theta(0)| < \frac{(\sigma\beta - \alpha)}{K \cdot m} \text{ so that}$$

$$\phi(t) < \frac{(\sigma\beta - \alpha)}{K^2 \cdot m} \text{ on an}$$

interval  $0 \leq t \leq a$ ,  $a > 0$ .

The exponent on the right hand side of (8) is negative. Hence the result easily follows.

*Remark:*—The theorem holds good when the constant matrix A is replaced by a periodic matrix.

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ON THE ROLE OF OPERATORS AS OBSERVABLES IN QUANTUM  
THEORY-II

By

R. L. DASVARMA

*Department of Mathematics, L. S. College, Muzaffarpur*

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ABSTRACT

In this paper, which is a sequel to the part I, the case of observable which can have continuous range of values has been considered and operators corresponding to such observables have been formed with the help of statistical density operators. The correspondence between the observables and their measurable values on the one hand and operators and their eigen values on the other, is established.

Since the operators are formed so as to be hypermaximal, the question of the solvability of the eigen value problem for these operators does not arise.

1. In part I of this paper, it was shown that the correspondence between observables, their measurable values and their characteristic states on the one hand, and Hermitian operators in Hilbert space, their eigenvalues and their eigenvectors on the other, can be established from the correspondence between states and Hilbert vectors when the observables have discrete measurable values if we interpret the inner product between two vectors representing states as defining the transition probability between these states. In this part, these correspondences will be extended to the case of observables which can have a continuous range of values.

In the case of an observable with continuous range of values, we first note that states are represented by square-integrable functions forming the Hilbert space  $L_2$ . Such observables are continuous random variables and if  $\psi(x)$  denotes a state,  $x$  being an observable with continuous values,  $|\psi(x)|^2$  is the density of probability that a measurement will yield the value  $x$  of this observable. If  $\phi_1(x)$  and  $\phi_2(x)$  represent two states characteristic of an observable A with values  $a_1$  and  $a_2$ ,  $\phi_1(x)$  and  $\phi_2(x)$  are mutually orthogonal. The various states characteristic of the observable A correspond to functions forming a complete orthonormal sequence  $\{\phi_i(x)\}$  in  $L_2$ .

The inner product in  $L_2$  is defined by

$$(1.1) \quad (\phi(x), \psi(x)) = \int_{-\infty}^{\infty} \phi^*(x) \psi(x) dx$$

for any two functions  $\phi(x)$  and  $\psi(x)$  and the probability of transition from the state  $\psi(x)$  to the state  $\phi(x)$  is

$$\left| \int_{-\infty}^{\infty} \phi^*(x) \psi(x) dx \right|^2.$$

An arbitrary state  $\psi(x)$  is the linear superposition

$$(1\cdot2) \quad \psi(x) = \sum_i c_i \phi_i(x), \quad c_i = \int_{-\infty}^{\infty} \phi_i^*(x) \psi(x) dx,$$

the transition probabilities from the state  $\psi(x)$  to the different states  $\phi_i(x)$  being  $|c_i|^2$ . Therefore,

$$(1\cdot3) \quad \int_{-\infty}^{\infty} |\psi(x)|^2 dx = \sum_i |c_i|^2 = 1.$$

2. Let  $\psi(x)$  represent a state. The integral operator whose kernel is

$$(2\cdot1) \quad \rho(x, x') = \psi(x) \psi^*(x'),$$

is the statistical density operator of von Neumann for the state  $\psi(x)$ . The kernel is evidently Hermitian. Further, symbolically, we have

$$(2\cdot2) \quad \rho^2(x, x'') = \int_{-\infty}^{\infty} \rho(x, x') \rho(x', x'') dx' = \int_{-\infty}^{\infty} \psi(x) \psi^*(x') \psi(x') \psi^*(x'') dx'$$

$$= \psi(x) \psi^*(x'') = \rho(x, x''),$$

since by (1·3)  $\int_{-\infty}^{\infty} \psi(x') \psi^*(x') dx' = 1$ .

Therefore,  $\rho(x, x')$  is the kernel of a Hermitian idempotent integral operator.

As von Neumann has shown, in transition from the Hilbert space of vectors to the Hilbert space  $L_2$  of square-integrable functions,  $\sum_{-\infty}^{\infty} \dots$  is replaced by  $\int_{-\infty}^{\infty} \dots dx$ .

For the trace of  $\rho(x, x')$ , we have

$$(2\cdot3) \quad \text{tr } \rho(x, x') = \int_{-\infty}^{\infty} \rho(x, x) dx = \int_{-\infty}^{\infty} \psi(x) \psi^*(x) dx = 1.$$

From (2·2) and (2·3) we see that  $\rho(x, x')$  is a projection of trace equal to unity. If  $\phi(x)$  be any state, we have

$$(2\cdot4) \quad \int_{-\infty}^{\infty} \rho(x, x') \phi(x') dx' = \int_{-\infty}^{\infty} \psi(x) \psi^*(x') \phi(x') dx' = (\psi(x), \phi(x)) \psi(x),$$

Therefore  $\rho(x, x')$  projects an arbitrary state  $\phi(x)$  into the state  $\psi(x)$ .

3. A state in which  $x$  has the value  $x'$  can be suitably represented by Dirac's delta function,  $\delta(x - x')$  where

$$(3.1) \quad \delta(x - x') = 0, \quad x \neq x', \quad \int_{-\infty}^{\infty} \delta(x - x') dx = 1.$$

This is not a proper function being undefined for  $x = x'$ , but is really a measure. Its properties are well-known and it is frequently used to replace the Krönecker delta symbol in transition from discrete indices to continuous variables.

The delta-function is also the kernel of an integral operator, as can be seen from the relation

$$(3.2) \quad \int_{-\infty}^{\infty} f(x) \delta(x - x') dx = f(x'),$$

for any regular function  $f(x')$ .

Since we have

$$(3.3) \quad \int_{-\infty}^{\infty} \delta(x - x') \delta(x - x'') dx = \delta(x' - x''),$$

the two states represented by  $\delta(x - x')$  and  $\delta(x - x'')$ , corresponding to different values  $x'$  and  $x''$ , are mutually orthogonal.

The statistical operator for the state  $x = x'$  is the integral operator whose kernel is  $\delta(x - x')$ . Since

$$(3.4) \quad \int_{-\infty}^{\infty} \delta(x - x') \delta(x' - x'') dx' = \delta(x - x''),$$

this integral operator is a projection and on account of its property (3.1), its trace is unity. Further, for different values of  $x'$ , it determines a family of mutually orthogonal projections of unit trace and therefore, constitutes a resolution of the identity.

A Hermitian operator defined by

$$(3.5) \quad X = \int_{-\infty}^{\infty} x' \delta(x - x') dx' = x,$$

has the following properties :

- (a) The above resolution of the identity belongs to it.
- (b) It has a continuous range of eigenvalues  $x'$ ,
- (c) Its eigenfunctions are the improper delta-functions.

This operator corresponds to the observable  $x$  and has as its eigenvalues, the continuous range of values  $x'$  of the observable  $x$ .

From (3.5) it is evident that this operator is the same as the number  $x$  and its operation on a function representing a state is simple multiplication by the number  $x$ .

4. Let  $k$  be any observable having a continuous range of values and let  $\psi(x; k)$  represent the characteristic states of this observable, for different values of  $k$ . The linear Hermitian integral operator whose kernel is  $\psi(x; k)\psi^*(x'; k)$  is the statistical density operator for the state  $\psi(x; k)$ . Denoting this kernel by

$$(4.1) \quad \rho(x, x'; k) = \psi(x; k)\psi^*(x'; k),$$

we have a family of mutually orthogonal projections, for which the trace

$$(4.2) \quad \text{tr} \rho(x, x'; k) = \int_{-\infty}^{\infty} \rho(x, x; k) dx = \int_{-\infty}^{\infty} \psi(x; k)\psi^*(x; k) dx = 1.$$

Also

$$(4.3) \quad \int_{-\infty}^{\infty} \rho(x, x; k) dk = 1.$$

Hence this family of projections constitute a resolution of the identity belonging to the Hermitian operator

$$(4.4) \quad K = \int_{-\infty}^{\infty} k \rho(x, x'; k) dk.$$

For this operator, we have

$$(4.5) \quad \left\{ \begin{array}{l} K \psi(x; k') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} k \psi(x; k) \psi^*(x'; k) \psi(x'; k') dx' dk \\ = \int_{-\infty}^{\infty} k \psi(x; k) \int_{-\infty}^{\infty} \psi^*(x'; k) \psi(x'; k') dx' dk \\ = \int_{-\infty}^{\infty} k \psi(x; k) \delta(k - k') dk = k' \psi(x; k'), \end{array} \right.$$

showing that  $\psi(x; k')$  are eigenfunctions of  $K$  belonging to eigen values  $k'$

Now, in the state  $\psi(x)$ , the expectation of  $k$  is

$$(4 \cdot 6) \quad \bar{k} = \int_{-\infty}^{\infty} k |\phi(k)|^2 dk,$$

where

$$(4 \cdot 7) \quad \left\{ \begin{array}{l} \phi(k) = \int_{-\infty}^{\infty} \psi^*(x; k) \psi(x) dx, \\ \psi(x) = \int_{-\infty}^{\infty} \phi^*(k) \psi(x; k) dk. \end{array} \right.$$

Thus

$$\begin{aligned} \bar{k} &= \int_{-\infty}^{\infty} k \phi^*(k) \phi(k) dk = \int_{-\infty}^{\infty} k \phi^*(k) \int_{-\infty}^{\infty} \psi^*(x'; k) \psi(x') dx' dk \\ &= \int_{-\infty}^{\infty} k \int_{-\infty}^{\infty} \psi(x; k) \psi^*(x) dx \int_{-\infty}^{\infty} \psi^*(x'; k) \psi(x') dx' dk \\ &= \int_{-\infty}^{\infty} \psi^*(x) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} k \psi(x; k) \psi^*(x'; k) \psi(x') dx' dk dx \\ &= (\psi(x), K \psi(x)). \end{aligned}$$

All the correspondences are thus established.

5. The solvability of the eigenvalue problem for Hermitian operators in Hilbert space is a very difficult question and von Neumann has proved that the solution rests on whether there exists a resolution of the identity belonging to the Hermitian operator and whether this resolution is unique. He has defined the operator for which the solution of the eigenvalue problem exists and is unique, as a hypermaximal operator. In the method of formation of the operator corresponding to observables, which we have followed here, this question does not arise because the operators are so formed that the eigenvalue problem is always solvable.

KINETIC ENERGY END CORRECTION FOR NEWTONIAN AND  
NON-NEWTONIAN FLUID FLOWS IN THE INLET LENGTH  
OF AN ANNULUS

By

J. N. KAPUR

*Indian Institute of Technology, Kanpur* and

R. R. DIKSHIT

*V. S. S. D. College, Kanpur*

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ABSTRACT

Formulae for the pressure drop in the inlet length of an annulus for the flows of power-law and Bingham plastic fluids have been obtained by the kinetic energy end correction method. Formulae for the flows of (i) Newtonian fluids in an annulus and of (ii) non-Newtonian fluids in circular pipes and straight channels, have been obtained as particular cases.

1. INTRODUCTION

A first approximation to the difference between the pressure at the entry of a pipe or channel and the pressure at the end of the inlet length i. e. at the position where the final velocity distribution may be said to be attained may be obtained by the so-called kinetic energy end-correction method. For Newtonian fluids this correction is well known and has been discussed in Goldstein (1) both for a circular pipe and a rectangular channel. A systematic account of the kinetic energy end correction both for circular and straight channels for a number of non-Newtonian fluids has been recently given by Kapur and Gupta (2).

In the present paper we extend their treatment to the case when the flow takes place in an annulus between two coaxial cylinders and obtain formulae for the pressure drop for power-law and Bingham plastic fluid flows. Formulae for the flows of (i) Newtonian fluids in an annulus and of (ii) Non-Newtonian fluids in circular pipes and straight channels, have been obtained as particular cases.

2. POWER-LAW FLUID FLOWS :

The rheological equation for these fluids is given by [3].

$$\Gamma_{ij} = k \left| \left( \sum_{m=1}^3 \sum_{l=1}^3 \epsilon_{lm} \epsilon_{ml} \right)^{\frac{n-1}{2}} \right| \epsilon_{ij}, \quad (1)$$

where  $\Gamma_{ij}$  and  $\epsilon_{ij}$  are the components of stress and strain-rate tensors respectively and  $k$  and  $n$  are the consistency and flow behaviour indices respectively. For fully developed flow in the annulus between two coaxial cylinders we get

$$\Gamma_{rz} = \mu \left| \epsilon_{rz} \right|^{\frac{n-1}{2}} \epsilon_{rz} = \mu \left| \frac{\partial u}{\partial r} \right|^{\frac{n-1}{2}} \frac{\partial u}{\partial r}, \quad (2)$$

where  $\Gamma_{rs}$  and  $\varepsilon_{rs}$  are non-zero components of stress and strain-rate tensors.

$\mu = k \cdot 2^{\frac{n-1}{2}}$  and  $u$  is the velocity at any point  $(r, \theta, z)$  of the annulus between the coaxial cylinders of radii  $KR$  and  $R$  (where  $k < 1$ ). Let  $\lambda R$  be the radial distance of those points from the axis of cylinders where the shear stress is zero.

Fredrikson and Bird (4) have discussed the flow of this fluid in an annulus and they have obtained the following expressions for the velocity distribution :

$$u = \left( \frac{PR}{2\mu} \right)^s R \int_k^\rho \left( \frac{\lambda^2}{\rho} - \rho \right)^n d\rho, \quad k \leq \rho \leq \lambda \quad (3)$$

$$u = \left( \frac{PR}{2\mu} \right)^s R \int_\rho^1 \left( \rho - \frac{\lambda^2}{\rho} \right)^s d\rho, \quad \lambda \leq \rho \leq 1 \quad (4)$$

where

$$\rho = \frac{r}{R}, \quad s = \frac{1}{n}, \quad P = - \frac{\partial p}{\partial z} \quad (6)$$

Since the above two velocities are equal at  $\rho = \lambda$ , we get

$$\int_k^\lambda \left( \frac{\lambda^2}{\rho} - \rho \right)^s d\rho = \int_\lambda^1 \left( \rho - \frac{\lambda^2}{\rho} \right)^s d\rho \quad (6)$$

If the fluid is pseudoplastic,  $n < 1$  and  $s > 1$ . If  $s$  is a positive integer, equation (6) may be expressed as

$$\sum_{i=0}^s \Lambda_{si} \lambda^{2i} + \Lambda_s \lambda^{s+1} = 0, \quad s=1, 2, 3, \dots \quad .. (7)$$

in which  $i \neq \frac{s+1}{2}$  and where

$$\Lambda_{si} = \frac{\binom{s}{i} (-1)^{i+1}}{s-2i+1} \left[ 1 + (-1)^s k^{s-2i+1} \right] \quad (8)$$

$$\Lambda_s = \left( \frac{s-1}{2} \right) (-1)^{\frac{s-1}{2}} \log \frac{1}{k}, \quad [s \text{ odd}] \quad (9)$$

$$\Lambda_s = 2 \sum_{i=0}^{\frac{s}{2}} \frac{\binom{s}{i} (-1)^i}{s-2i+1}, \quad [s \text{ even}] \quad (10)$$

From (7) we can determine  $\lambda$  as a function of  $s$  and  $k$ . The flux  $Q$  per unit time across any section of the annulus when the flow is fully developed is given by

$$Q = \pi R^3 \left( \frac{PR}{2\mu} \right)^s \left[ \sum_{i=0}^{s+1} E_{si} \lambda^{2i} + E_s \lambda^{s+3} \right], \quad (11)$$

in which  $i \neq \frac{s+3}{2}$  and where

$$E_{si} = \binom{s+1}{i} \frac{(-1)^i}{s-2i+3} \left[ 1 - (-1)^{s+1} k^{s-2i+3} \right], \quad (12)$$

$$E_s = \binom{s+1}{\frac{s-1}{2}} (-1)^{s-1} \log k^{-1}, [s \text{ odd}] \quad (13)$$

$$E_s = 2 \sum_{i=0}^{s+1} (-1)^i \binom{s+1}{i} \frac{1}{2i-s-3}, [s \text{ even}] \quad (14)$$

The results (11) and (13) differ slightly from those of Fredrikson and Bird (4), possibly due to some misprints in their paper.

The mean velocity  $u_m$ , which due to continuity of the flow may be treated as the entrance velocity also, may be expressed as

$$u_m = \frac{Q}{\pi R^2 (1-k^2)} = \frac{1}{1-k^2} R \left( \frac{PR}{2\mu} \right)^s \left[ \sum_{i=0}^{s+1} E_{si} \lambda^{2i} + E_s \lambda^{s+3} \right] \quad (15)$$

in which  $i \neq \frac{s+3}{2}$

Now for finding the pressure drop in the entry length, we make use of the kinetic energy end correction viz we assume that the loss of energy due to dissipation in the inlet length of the channel is the same as the dissipation of energy in the same length of the fully developed flow. This assumption is known to give fairly satisfactory results for the pressure drop in entry lengths in pipes and channels.

If  $P_0$  and  $P_L$  are the pressures at the beginning and end of inlet length  $L$ , the dissipation of energy in the inlet length

$$\begin{aligned} &= \pi R^3 (1-k^2) P_0 u_m - P_L 2\pi \int_{kR}^R u^3 dr + \frac{\rho_0 \pi}{2} R^2 (1-k^2) u_m^3 \\ &\quad - \pi \rho_0 \int_{kR}^R u^3 r dr \end{aligned}$$

$$= \pi R^2 (1 - k^2) u_m (P_o - P_L) + \frac{1}{2} \pi P_o R^2 u_m^3 (1 - k^2) \quad (16)$$

$$= \pi \rho_o R^2 \int_k^1 u^3 \rho d\rho$$

where  $\rho_o$  is the fluid density.

Also the dissipation of energy in the same length of the fully developed flow

$$= - \frac{\partial p}{\partial z} \pi R^2 (1 - k^2) L u_m \quad (17)$$

Equating these two, we get

$$\frac{P_o - P_L}{\frac{1}{2} \rho_o u_m^2} + 1 - \frac{2}{1 - k^2} \int_k^1 \left( \frac{u}{u_m} \right)^3 \rho d\rho = - \frac{\partial p}{\partial z} \frac{L}{\frac{1}{2} \rho_o u_m^2} \quad (18)$$

Using (3), (4), (15) and (18) and simplifying, we get

$$\frac{P_o - P_L}{\frac{1}{2} \rho_o u_m^2} = - \frac{32L/R}{R_n} + \chi_n, \quad (19)$$

where

$$R_n = \frac{8 \rho_o u_m}{\mu} \frac{2-1/s}{(1-k^2)^{1/s}} \frac{R^{1/s}}{\left[ \sum_{i=0}^{s+1} E_{si} \lambda^{2i} + E_s \lambda^{s+3} \right]^{1/s}}, \quad (20)$$

in which  $i \neq \frac{s+3}{2}$ ,

and

$$\begin{aligned} \chi_n = & -1 + 2(1-k^2)^2 \left[ \int_k^\lambda \rho \left\{ \int_k^\rho \left( \frac{\lambda^2}{\rho} - \rho \right)^s d\rho \right\}^3 d\rho \right. \\ & \left. + \int_\lambda^1 \rho \left\{ \int_\rho^1 \left( \rho - \frac{\lambda^2}{\rho} \right)^s d\rho \right\}^3 d\rho \right] \\ & \times \frac{1}{\sum_{\substack{i=0 \\ i \neq \frac{s+3}{2}}}^{s+1} \left[ E_{si} \lambda^{2i} + E_s \lambda^{s+3} \right]^3} \end{aligned} \quad (21)$$

For given values of  $k$  and  $s$ ,  $R_a$  and  $\chi_a$  can be evaluated. The corresponding value of  $\lambda$  can be obtained from the tables of Fredrikson and Bird [4]. We discuss some special cases below:

### 3. SPECIAL CASES

#### 3.1. Newtonian fluid flows in an annulus.

By putting  $s = 1$  in (7), (20) and (21), and simplifying we get

$$\Lambda_{10} + \Lambda_1 \lambda^2 = 0, \quad \Lambda_{10} = -\frac{1-k^2}{2}, \quad \Lambda_1 = \log k^{-1},$$

so that

$$\lambda^2 = \frac{1-k^2}{2 \log k^{-1}} \quad (22)$$

From equations (12), (13) and (20) and (21) we get

$$E_{10} = \frac{1-k^4}{4}, \quad E_{11} = -(1-k^2), \quad E_1 = \log k^{-1} \quad (23)$$

$$R_1 = \frac{8 \rho_o u_m}{\mu} R \left[ \frac{1+k^2}{4} - \lambda^2 + \frac{\log k^{-1} \lambda^4}{1-k^2} \right] \quad (24)$$

$$\begin{aligned} \chi_1 = & -1 + 2(1-k^2)^2 \left[ \int_k^\lambda \rho \left\{ \left( \frac{\lambda^2}{\rho} - \rho \right) d\rho \right\}^3 \right. \\ & + \left. \int_\lambda^1 \rho \left\{ \int_\rho^1 \left( \rho - \frac{\lambda^2}{\rho} \right) d\rho \right\}^3 \right] \\ & \times \frac{1}{(E_{10} + E_{11} \lambda^2 + E_1 \lambda^4)^3} \end{aligned} \quad (25)$$

By putting the value of  $\lambda_2$  from (22) and values of  $E_{10}$ ,  $E_{11}$ ,  $E_1$  from (23) in (24) and (25) we get

$$R_1 = \frac{2 \rho_o u_m R}{\mu} \left[ 1+k^2 - \frac{1-k^2}{\log k^{-1}} \right] = \frac{R_e}{1-k} \left[ 1+k^2 - \frac{1-k^2}{\log k^{-1}} \right] \quad (26)$$

and

$$\chi_1 = -1 + \frac{16}{\left[ 1+k^2 - \frac{1-k^2}{\log k^{-1}} \right]^3}$$

$$\chi_1 \left\{ \frac{1+k^2+k^4+k^6}{8} - \frac{11}{24} \left( \frac{1-k^2}{\log k^{-1}} \right) (1+k^2+k^4) \right. \\ \left. + \frac{21}{32} \left( \frac{1-k^2}{\log k^{-1}} \right)^2 (1+k^2) - \frac{3}{8} \left( \frac{1-k^2}{\log k^{-1}} \right)^3 \right\} \quad (27)$$

where

$$Re = \frac{2 R (1-k) u_m}{v} \quad (28)$$

Thus for Newtonian fluid flow in an annulus

$$\frac{P_o - P_L}{\frac{1}{2} \rho_0 u_m^2} = \frac{32 L/R}{R_1} + \chi_1 , \quad (29)$$

where  $R_1$  and  $\chi_1$  are given by equation (26) and (27). When  $k \rightarrow 0$ , this gives

$$\frac{P_o - P_L}{\frac{1}{2} \rho_0 u_m^2} = \frac{32 L/R}{Re} + 1 , \quad (30)$$

which agrees with the result for a circular pipe given by Goldstein (1).

Similarly by putting

$$\frac{\rho R}{kR} = \frac{kR+h+y}{kR} = 1 + \frac{h}{kR} \left( 1 + \frac{y}{h} \right) \quad (31)$$

and making  $R \rightarrow \infty$ , we get the result for flow in a straight channel given in (1)

### 3.2 Pseudoplastic fluid flow with $n = \frac{1}{2}$ in an annulus and a pipe :

In this case

$$\chi_2 = -1 + 2 (1-k^2)^2 \left[ \log k (3\lambda^{12} k^{-1} + 6\lambda^{10} k - \lambda^8 k^3) \right. \\ \left. + \frac{\lambda^{14}}{2} (k^{-3}+1) - \frac{24}{5} \lambda^{13} (k^{-2}+1) + \frac{99}{8} \lambda^{12} (k^{-1}+1) \right. \\ \left. - \frac{39104}{693} \lambda^{11} + \frac{129}{4} \lambda^{10} (k+1) - 16\lambda^9 (k^2+1) \right. \\ \left. + \frac{101}{120} \lambda^8 (k^3+1) + \frac{32}{5} \lambda^7 (k^4+1) - \frac{253}{90} \lambda^6 (k^5+1) - \frac{8}{15} \lambda^5 (k^6+1) \right]$$

$$+ \frac{129}{168} \lambda^4 (k^7 + 1) - \frac{17}{180} \lambda^2 (k^9 + 1) + \frac{3}{440} (k^{11} + 1) ] \\ \div [ \lambda^8 (1 + k^{-1}) - \frac{32}{5} \lambda^5 + 3\lambda^4 (1 + k) - \lambda^2 (1 + k)^3 + \frac{1 + k^5}{5} ]^3 \quad (32)$$

Values of  $\lambda$  for various values of  $k$  are given in (4).

When  $k \rightarrow 0$ , we get the values

$$R_2 = \frac{8\rho_o u_m^{3/2} R^{1/2}}{\sqrt{5\mu}}, \quad \lambda_2 = \frac{31}{44}, \quad (33)$$

obtained by Kapur and Gupta (2).

#### 4. BINGHAM PLASTIC FLUID FLOWS

The empirical equation for these fluids is

$$\Gamma_{rz} = T_o + \mu \frac{\partial u}{\partial r}, \text{ when } kR \leq r \leq \lambda R \quad (34)$$

and

$$\Gamma_{rz} = -\Gamma_o + \mu \frac{\partial u}{\partial r} \text{ when } \lambda R \leq r \leq R \quad (35)$$

If  $\lambda_- R$  and  $\lambda_+ R$  are the inner and outer radii of the plug region and if we use the dimensionless quantities

$$\frac{2\Gamma_{rz}}{PR} = T, \quad \frac{2\Gamma_o}{PR} = T_o, \quad \left( \frac{2\mu}{PR^2} \right) u = \phi, \quad \frac{r}{R} = \rho, \quad (36)$$

then from Fredrikson and Bird (4), we get

$$\lambda^2 = \lambda_- \lambda_+ \quad (37)$$

i.e.  $\lambda_-$ ,  $\lambda$  and  $\lambda_+$  are in geometrical progression

$$\lambda_- = \lambda_+ - T_o \quad (38)$$

$$\phi_- = -T_o(\rho - k) - \frac{1}{2}(\rho^2 - k^2) + \lambda^2 \log \frac{\rho}{k}, \quad (39)$$

$$k \leq \rho \leq \lambda_-$$

$$\phi_+ = -T_o(1 - \rho) + \frac{1}{2}(1 - \rho^2) + \lambda^2 \log \rho, \quad (40)$$

$$\lambda_+ \leq \rho \leq 1$$

The volume rate of flow,  $Q$  across any section of the annulus is

$$Q = \frac{\pi R^4 \rho}{8\mu} \left[ (1 - k^4) - 2\lambda_+ (\lambda_+ - T_o) (1 - k^2) - \frac{4}{3} (1 + k^3) T_o + \frac{1}{3} (2\lambda_+ - T_o)^3 T_o \right] \quad (41)$$

And the plug velocity of the fluid, say  $\phi_o$  is

$$\phi_o = (\phi_-)_\rho = \lambda_- = (\phi_+)_\rho = \lambda_+ \quad (42)$$

Hence the mean velocity  $u_m$ , which may be taken as the entrance velocity also, is

$$\begin{aligned} u_m &= \frac{Q}{\pi R^2 (1 - k^2)} \\ &= \frac{PR^2}{1 - k^2} \left[ 1 - k^4 - 2\lambda_+ (\lambda_+ - T_o) (1 - k^2) \right. \\ &\quad \left. - \frac{4}{3} (1 + k^3) T_o + \frac{1}{3} (2\lambda_+ - T_o)^3 T_o \right] \end{aligned} \quad (43)$$

And the pressure drop equation (16) in this case may be stated as

$$\begin{aligned} \frac{P_o - P_L}{\frac{1}{2} \rho_o u_m^2} &= -1 + \frac{PL}{\frac{1}{2} \rho_o u_m^2} + \frac{2}{1 - k^2} \int_k^1 \left( \frac{u}{u_m} \right)^3 \rho d\rho \\ &= \frac{32 L/R}{R_n} + \chi^1, \end{aligned} \quad (44a)$$

where

$$\begin{aligned} R_n' &= \frac{16 \rho_o u_m^2}{PR} = \frac{2\rho_o u_m R}{\mu (1 - k^2)} \left[ 1 - k^4 + 2\lambda_+ (1 - k^2) \right. \\ &\quad \left. + \Gamma_o \left\{ 2\lambda_+^2 (1 - k^2) - \frac{4}{3} (1 - k^3) + \frac{8}{3} \lambda_+^3 \right\} \right. \\ &\quad \left. + 2 T_o^3 \lambda_+ - \frac{1}{3} T_o^4 - 4 T_o^2 \lambda_+^2 \right] \end{aligned} \quad (44b)$$

and

$$\begin{aligned} \chi' &= -1 + \frac{2}{1 - k^2} u^3 (1 - k^2)^3 \left[ -\frac{3}{2} \phi_o^2 T_o \left\{ \frac{\lambda_-^2}{2} (T_o - 2\lambda_+) \right. \right. \\ &\quad \left. \left. - \frac{1}{3} \lambda_+^3 (1 - k^3) + \frac{8}{3} \lambda_+^4 \right\} \right] \end{aligned}$$

$$\begin{aligned}
& - \frac{1}{3} (2\lambda_+ - \Gamma_o) (\lambda_+^2 - \lambda_+ \Gamma_o + \Gamma_o^2) - \frac{1}{4} (-4\lambda_+^3 + 6\lambda_+^2 \Gamma_o - 4\lambda_+ \Gamma_o^2 + \Gamma_o^3) \Big\} \\
& + 3\phi_o \left\{ \frac{\lambda^2}{4} (\lambda_-^2 - \lambda_+^2) - \frac{3\lambda^2}{16} (\lambda_-^4 - \lambda_+^4) + \frac{1}{24} (\lambda_-^6 - \lambda_+^6) \right. \\
& \quad \left. + \Gamma_o \left( \frac{7}{60} \overline{\lambda_-^5 + \lambda_+^5} - \frac{5}{18} \lambda^2 \overline{\lambda_-^3 + \lambda_+^3} \right) + \frac{\Gamma_o^2}{12} (\lambda_-^4 - \lambda_+^4) \right\} \\
& - 3 \left\{ \frac{\lambda^6}{8} (\lambda_-^2 - k^2 + 1 - \lambda_+^2) - \frac{7}{64} \lambda^4 (\lambda_-^4 - k^4 + 1 - \lambda_+^4) \right. \\
& \quad \left. + \frac{11}{288} \lambda^2 (\lambda_-^6 - k^6 + 1 - \lambda_+^6) - \frac{1}{192} (\lambda_-^8 - k^8 + 1 - \lambda_+^8) \right\} \\
& + \Gamma_o \left\{ \frac{19}{108} \lambda^4 (\lambda_-^3 - k^3 + 1 - \lambda_+^3) - \frac{419}{3600} \lambda^2 (\lambda_-^5 - k^5 + 1 - \lambda_+^5) \right. \\
& \quad \left. + \frac{19}{840} (\lambda_-^7 - k^7 + 1 - \lambda_+^7) \right\} \\
& + \Gamma_o^2 \left\{ \frac{13}{144} \lambda^2 (\lambda_-^4 - k^4 + 1 - \lambda_+^4) - \frac{1}{13} (\lambda_-^6 - k^6 + 1 - \lambda_+^6) \right\} \\
& t \frac{\Gamma_o^3}{60} \left\{ \lambda_-^5 - k^5 + 1 - \lambda_+^5 \right\} \Big] \\
& \div \left[ 1 - k^4 - 2\lambda_+^2 (1 - k^2) + \Gamma_o \left\{ 2\lambda_+ (1 - k^2) - \frac{4}{3} (1 + k^2) + \frac{8}{3} \lambda_+^3 \right\} \right]^3 \quad (45) \\
& \quad + \Gamma_o^2 (-4\lambda_+^2) + 2\lambda_+ \Gamma_o^3 - \frac{1}{2} \Gamma_o^4 \Big]^3
\end{aligned}$$

## 5. PARTICULAR CASES FROM BINGHAM PLASTIC FLOW :

### 5.1 Bingham Fluid Flowing through a circular pipe :

Putting  $k = 0$  and so  $\lambda_- = \lambda = 0$  in (38) and (40) we get respectively

$$\lambda_+ = \Gamma_o \quad (46)$$

and

$$\phi_- = \frac{(1 - T_o)^2}{2} \quad (47)$$

And consequently by putting these values in (44) and (45) we get

$$R' = \frac{2\rho_0 u_m R}{3\mu (1+k)} (1 - T_0) (3 + 2T_0 + T_0^2) \quad (48)$$

$$\chi^1 = \frac{54}{35} \frac{35 + 58 T_0 + 47 T_0^2}{(3 + 2 T_0 + T_0^2)^3}, \quad (49)$$

which are the values for Bingham fluid flow through a circular pipe obtained by Kapur and Gupta (2).

### 5.2 Newtonian Fluid flowing through an annulus :

Putting  $\Gamma_0 = 0$  and so  $\lambda_- = \lambda_+ = \lambda$  in (39) and (40) and equating  $\phi_-$  and  $\phi_+$  we get

$$\lambda^2 = \frac{1-k^2}{2 \log k^{-1}}$$

which is the equation (22) obtained earlier.

Again with this value of  $\lambda^2$  and by applying the condition  $\Gamma_0 = 0$  and  $\lambda_- = \lambda_+ = \lambda$  in (44) and (45), we get the corresponding equation for Newtonian fluids.

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# POLARIMETRIC ESTIMATION OF COPPER

By

O. N. PERTI and I. PRAKASH

Chemical Laboratories, Th. D. S. B. Government College, Nani Tal, U. P.

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## ABSTRACT

By adding an excess amount of potassium iodide to copper salt solution, it is transformed into complex iodo compound which is precipitated by addition of quinine sulphate solution. The optically active copper-quinine-compound is filtered, washed, dissolved in acetone and determined polarimetrically using following empirical formula.

$$W = 12.26 R - 1.1642 \text{ mgs/50 ml}$$

where  $W = \text{Cu}^{++} \text{ mgs/50 ml}$  and  $R$  is the angle of rotation in degrees.

## INTRODUCTION

Several optically active nitrogenous compounds such as alkaloids have been used in analytical procedures for the determination of metallic ions.

Recently Liteanu and Cosma<sup>1</sup> have described polarimetric estimation of Hg(II) ions by first converting it into tetra-iodo-mercurate with the help of potassium iodide and then precipitating it with quinine mono-chloro-hydrate solution. The properly washed quinine complex, thus obtained, was dissolved in acetone and estimated polarimetrically with the help of an empirical equation derived experimentally. This method was extended by us<sup>2</sup> in the case of polarimetric estimation of cadmium. In the present communication we have described the polarimetric estimation of copper along similar lines.

Karenman<sup>3,4</sup> used brucine and quinine for the detection of copper in conjunction with potassium iodide. He reported the sensitivity of copper reaction as 1 : 300,000 for brucine and 1 : 900,000 for quinine. Due to high sensitivity of latter reaction, the authors have employed quinine sulphate along with potassium iodide for the quantitative precipitation of copper(II) in the form of optically active compound. The procedure involves conversion of Cu(II) into iodo-compound which is precipitated as optically active compound by employing quinine sulphate solution as precipitant. The precipitate is filtered, washed, dissolved in acetone and optical rotation is measured by means of polarimeter.

## EXPERIMENTAL

Following solutions were used in connection with polarimetric estimation of Cu(II) :—

(i) Solution of copper sulphate (A. R., B. D. H.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) of concentration 1.272 mgs of Cu(II)/ml.

- (ii) Saturated solution of potassium-iodide.
- (iii) 3% solution of quinine sulphate containing a few drops of concentrated sulphuric acid.

An excess amount of potassium-iodide was added to an aliquot of copper sulphate solution. The colour of liberated iodine was discharged by adding a few drops of sulphurous acid. To the resulting colourless solution of cupro-iodide complex, slight excess of quinine sulphate was added. It was observed that 120 mgs of quinine sulphate was quite sufficient for quantitative precipitation of 5 mgs of Cu(II). The beaker, containing yellow precipitate, was kept in ice for a few minutes as the precipitate was found slightly soluble at room-temperature. Precipitate was filtered, washed with ice-cold water and then dissolved in acetone. The orange coloured acetone solution of the copper quinine compound was rendered light yellow by first making it just ammoniacal and finally very slightly acidic by addition of a few drops of 0.25 N HCl. By this treatment the deep colour of the compound in acetone medium became light yellow and it made possible the polarimetric measurement from 2 mgs to 30 mgs of Cu(II)/50 ml. Volume of solution was made upto 50 ml with acetone and polarimetric measurement was carried out, using two decimeter tube, at room temperature ( $19^{\circ}\text{C}.$ ).

Results are given in Table 1. In Table 2, polarimetric estimations for copper have been compared with standard thiocyanate gravimetric method.

TABLE 1

*Optical rotations of solutions containing different amount of copper in the form of optically active compound.*

Serial No.	Copper ions/50 ml (mgs)	Optical rotation in degrees for Hg 5461
1	2.544	0.32
2	5.088	0.51
3	10.176	0.96
4	12.720	1.10
5	15.264	1.30
6	20.352	1.78
7	25.440	2.18
8	30.528	2.58

### DISCUSSION

A plot of concentration against optical rotation shows a linear relationship (Fig. 1).

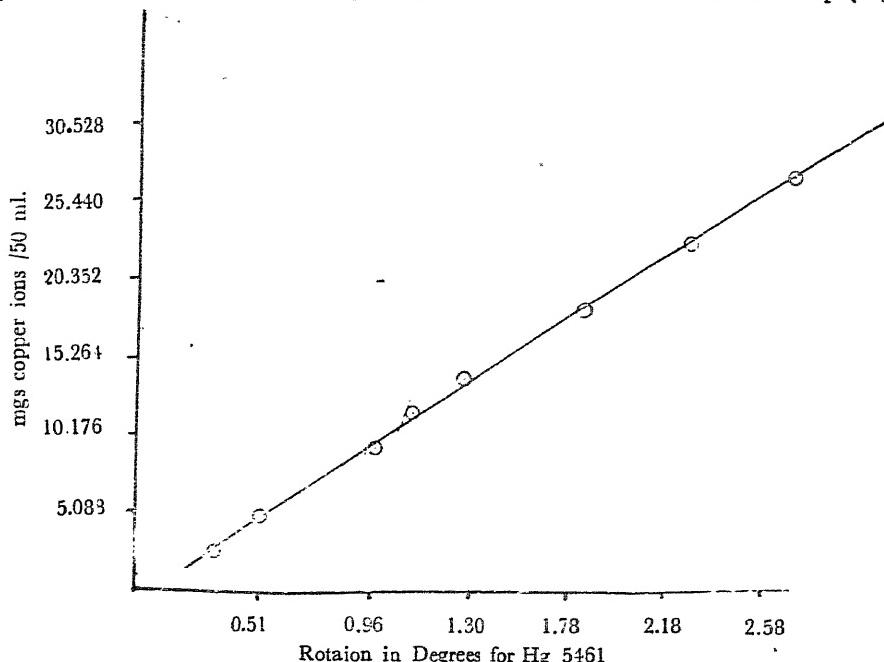


Fig. 1. Graph showing relationship between optical rotation and concentration.

The equation for the curve was calculated by the method of least squares and following expression was obtained.

$$W = 12.26 R - 1.1642 \text{ mgs of copper /50 ml}$$

where W is the concentration of copper ions mgs/50 ml and R is the angle of rotation in degrees.

TABLE 2

Serial No.	Amount of copper (mgs)		Difference (a) — (b) mgs
	Gravimetrically estimated (a)	Polarimetrically estimated (b)	
1	2.544	2.7590	- 0.21
2	5.088	5.0884	0.00
3	10.176	10.6054	- 0.43
4	12.720	12.3418	+ 0.38
5	15.264	14.7738	+ 0.49
6	20.352	20.6586	- 0.31
7	25.440	25.5626	- 0.12
8	30.528	30.4660	+ 0.06

It is clear from Table 2 that polarimetric estimation of copper ions gives fairly accurate results. The accuracy of polarimetric method lies between 5 mgs to 30 mgs of copper ions per 50 ml.

#### CONCLUSION

The polarimetric method of estimating copper is fairly accurate and it can well be compared with the colorimetric methods of estimation<sup>5</sup>. This method has the advantage over colorimetric method of being quick and easy to perform. Its obvious advantage lies in routine and rapid estimation of metallic ions (Cu [II]). Its accuracy and sensitivity can be further increased by noting optical rotation in the spectral region of largest molecular rotation of active substance (say ultraviolet) and by employing an objective apparatus, that is, photoelectrical methods of recording rotations.

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# APPROXIMATE EVALUATION OF CERTAIN INTEGRALS

By

S. L. GUPTA

*Mathematics Department, University of Jodhpur, Jodhpur*

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## ABSTRACT

It is found that the Bessel functions of two arguments are useful for various applications. In a separate paper I have shown the application of these functions in problems connected with transformation, expansion and modifications.

The object of this note is to illustrate the application of the function  $J_m(x_1, x_2)$  in evaluation of certain integrals approximately.

The function  $J_m(x_1, x_2)$  is defined by

$$\frac{\frac{1}{2}x_1}{e} \left( u - \frac{1}{u} \right) + \frac{1}{2}x_2 \left( u^2 - \frac{1}{u^2} \right) = \sum_{m=-\infty}^{\infty} u^m J_m(x_1, x_2), \quad \dots \quad (1)$$

for all values of  $x_1$ ,  $x_2$  and  $u$ , except  $u=0$ .

In this, if we put  $u=e^{i\theta}$  and equate real and imaginary parts on both sides, we get

$$\cos(x_1 \sin\theta + x_2 \sin\theta) = \sum_{m=-\infty}^{\infty} \cos m\theta J_m(x_1, x_2),$$

$$\sin(x_1 \sin\theta + x_2 \sin 2\theta) = \sum_{m=-\infty}^{\infty} \sin m\theta J_m(x_1, x_2).$$

These are equivalent to

$$\cos(x_1 \sin\theta + x_2 \sin 2\theta) = J_0(x_1, x_2) + \sum_{m=1}^{\infty} \cos m\theta (J_m(x_1, x_2) + J_{-m}(x_1, x_2)), \quad (2)$$

$$\sin(x_1 \sin\theta + x_2 \sin 2\theta) = \sum_{m=1}^{\infty} \sin m\theta (J_m(x_1, x_2) - J_{-m}(x_1, x_2)). \quad \dots \quad (3)$$

From these equations we can show that

$$J_m(x_1, x_2) = \frac{1}{\pi} \int_0^{\pi} \cos(m\theta - x_1 \sin \theta - x_2 \sin 2\theta) d\theta, \quad \dots \quad (4)$$

evidently

$$| J_m(x_1, x_2) | < 1. \quad \dots \quad (5)$$

Taking  $a > 0$ , if we multiply (2) and (3) by  $\theta^n e^{-a\theta}$  respectively and integrate from 0 to  $\infty$  and evaluate integrals on the right, we get

$$\int_0^{\infty} \theta^n e^{-a\theta} \cos(x_1 \sin \theta + x_2 \sin 2\theta) d\theta = \frac{n!}{a^{n+1}} J_0(x_1, x_2) + n! \sum_{m=1}^{\infty} \left( \frac{(a-im)^{n+1} + (a+im)^{n+1}}{2(a^2 + m^2)^{n+1}} \right) (J_m(x_1, x_2) + J_{-m}(x_1, x_2)), \quad (6)$$

$$\int_0^{\infty} \theta^n e^{-a\theta} \sin(x_1 \sin \theta + x_2 \sin 2\theta) d\theta = i n! \sum_{m=1}^{\infty} \left( \frac{(a-im)^{n+1} - (a+im)^{n+1}}{2(a^2 + m^2)^{n+1}} \right) (J_m(x_1, x_2) - J_{-m}(x_1, x_2)), \quad (7)$$

where  $n=0, 1, 2, \dots$

If we multiply (2) by  $e^{-a^2\theta^2}$  and  $\frac{1}{1+\theta^2}$  respectively and integrate from 0 to  $\infty$ , then on evaluating the integrals on the right-hand side, we get

$$\int_0^{\infty} e^{-a^2\theta^2} \cos(x_1 \sin \theta + x_2 \sin 2\theta) d\theta = \frac{\sqrt{\pi}}{2a} J_0(x_1, x_2) + \frac{\sqrt{\pi}}{2a} \sum_{m=1}^{\infty} e^{-m^2/4a^2} (J_m(x_1, x_2) + J_{-m}(x_1, x_2)), \quad (8)$$

$$\int_0^{\infty} \frac{\cos(x_1 \sin \theta + x_2 \sin 2\theta)}{1+\theta^2} d\theta = -\frac{\pi}{2} J_0(x_1, x_2) + \frac{\pi}{2} \sum_{m=1}^{\infty} e^{-m^2/4a^2} (J_m(x_1, x_2) + J_{-m}(x_1, x_2)), \quad (9)$$

On multiplying (3) by  $\frac{1}{\theta}$  and integrating from 0 to  $\infty$ . And on putting the value of the integrals on the right-hand side, we obtain

$$\int_0^\pi \frac{\sin(x_1 \sin \theta + x_2 \sin 2\theta)}{\theta} d\theta = \frac{\pi}{2} \sum_{m=1}^{\infty} (J_m(x_1, x_2) - J_{-m}(x_1, x_2)). \quad (10)$$

If we multiply (2) by  $\frac{1}{a-b \cos \theta}$  for  $|a| > |b|$  and integrate from 0 to  $\pi$ ; then on using

$$\int_0^\pi \frac{\cos m\theta}{a-b \cos \theta} d\theta = \frac{\pi}{\sqrt{a^2-b^2}} \left( \frac{b}{a+\sqrt{a^2-b^2}} \right)^m,$$

we get

$$\int_0^\pi \frac{\cos(x_1 \sin \theta + x_2 \sin 2\theta)}{a-b \cos \theta} d\theta = \frac{\pi}{\sqrt{a^2-b^2}} J_0(x_1, x_2) + \frac{\pi}{\sqrt{a^2-b^2}} \sum_{m=1}^{\infty} \left( \frac{b}{a+\sqrt{a^2-b^2}} \right)^m \left( J_m(x_1, x_2) + J_{-m}(x_1, x_2) \right) \quad (11)$$

Similarly, from various evaluable definite integrals whose integrands are of the form  $\cos m\theta f(\theta)$  or  $\sin m\theta f(\theta)$ , we can find out numerous integrals having their integrands of the form  $\cos(x_1 \sin \theta + x_2 \sin 2\theta) f(\theta)$  or  $\sin(x_1 \sin \theta + x_2 \sin 2\theta) f(\theta)$ .

In the right-hand side expression of (6) to (11) the co-efficient of  $(J_m(x_1, x_2) \pm J_{-m}(x_1, x_2))$  decreases as  $m$  increases. Also, from (5) we have  $|J_m(x_1, x_2) \pm J_{-m}(x_1, x_2)| < 2$ , therefore, an approximate value of the integrals given on the left-hand side of the results from (6) to (11) can be found by taking a first few terms of the right-hand side series.

If  $x_1, x_2$  are small and it is sufficient to retain first and second degree terms only; then from (4) it can be seen that :

$$J_{\pm 1}(x_1, x_2) \approx \pm \frac{x_1}{2} - \frac{x_1 x_2}{4};$$

$$J_{\pm 2}(x_1, x_2) \approx \pm \frac{x_2}{2} + \frac{x_1^2}{8};$$

$$J_{\pm 3}(x_1, x_2) \approx \frac{x_1 x_2}{4};$$

$$J_{\pm 4}(x_1, x_2) \approx -\frac{x_2^2}{8} \quad \text{and}$$

$$J_{\pm m}(x_1, x_2) \approx 0, \quad \text{when } m > 4.$$

These results may be used in obtaining the approximate value of the above mentioned integrals. In general when numerical values of  $x_1$  and  $x_2$  are given then for better approximations we are required to substitute the values of  $J_m(x_1, x_2)$  and  $J_{-m}(x_1, x_2)$  from the tables.

Similarly, if we proceed from the definitions of the Bessel functions of several arguments and of integral orders, we shall obtain numerous results of the form (6) to (11). Accordingly, these results may be used to approximate the definite integrals occurring in them.

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# POLARIMETRIC ESTIMATION OF SILVER

By

O. N. PERTI and I. PRAKASH

*Chemical Laboratories, Th. D. S. B. Government College, Naini Tal, U. P.*

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## ABSTRACT

Polarimetric estimation of Ag(I) in aqueous solution is possible quite rapidly and with a fair degree of accuracy. First of all Ag(I) is converted into potassium-argento-iodide by adding an excess amount of potassium iodide. Complex-iodo compound is precipitated in the form of optically active silver-quinine compound by adding aqueous solution of quinine sulphate. The precipitate of optically active compound is filtered, washed, dissolved in acetone and estimated polarimetrically using following empirical equation.

$$W = 0.678 + 38.7 R \text{ mgs of Ag(I)/50 ml}$$

where  $W = \text{Ag (I) mgs/50 ml}$  and  $R$  is the angle of rotation in degrees.

## INTRODUCTION

Several optically active alkaloids have been used as sensitive reagents for detection as well as estimation of metallic ions. In their recent communication Liteanu and Gosma<sup>1</sup> have extended the use of quinine in the form of quinine-mono chloro hydrate solution for quantitative precipitation of Hg(II) from solution of tetra-iodo-mercurate as optically active compound. After filtration and proper washing, precipitate of optically active compound was dissolved in acetone. This solution was subjected to polarimetric measurement to record the angle of rotation. Amount of Hg(II) in a given volume of solution was then calculated by substituting rotation value in an empirical equation, based on experimental data. This method of polarimetric estimation of Hg(II) has been made by us as basis for determination of Cadmium<sup>2</sup> and bismuth<sup>3</sup> polarimetrically and has been further applied in case of Ag(I) as described here.

Solution of quinine salt along with potassium iodide has been employed by a large number of workers for the microchemical detection of small quantities of metals. For example Korenman<sup>4,5</sup> has used free base in conjunction with potassium iodide for detection of cadmium and reported that lead, Hg(II), bismuth, Cu(II) and antimony react similarly. Martini<sup>6</sup> has used quinine sulphate for the microchemical detection of small quantities of cadmium. Laporte<sup>7</sup> has used the orange-red colour which is formed in the reaction between quinine, potassium iodide and bismuth for the colorimetric determination of the latter. This led us to study the reaction of Ag(I) with quinine sulphate in conjunction with potassium iodide and we found the reaction to be fairly sensitive for quantitative precipitation of silver. Potassium-argento-iodide, resulting by adding saturated solution

of potassium iodide to silver salt solution, is precipitated in the form of optically active compound by addition of required amount of quinine sulphate.

#### EXPERIMENTAL

Following solutions were prepared in connection with polarimetric estimation of silver.

(i) Solution of silver nitrate (A. R., B. D. H.) of concentration 1.27 mgs of Ag(I)/ml was prepared in conductivity water.

(ii) Saturated solution of potassium iodide.

(iii) 3 : solution of quinine sulphate containing a few drops of concentrated sulphuric acid.

To an aliquot of silver nitrate solution, saturated solution of potassium iodide was added drop by drop till precipitate of silver iodide dissolved completely, yielding potassium argento iodide. Now iodo complex was treated with aqueous solution of quinine sulphate in slight excess resulting in the precipitation of optically active compound. It was noted that 27 mgs of quinine sulphate was quite sufficient for quantitative precipitation of 1 mg of silver (I). The precipitate, in beaker, was cooled in ice for sometime to ensure complete precipitation. It was separated by filtration and washed with a few ml of cold water. It was then dissolved in acetone and the volume was made upto 50 ml. Optical rotation of solution was measured as usual using 2 dcm tube at 18°C° (room temperature).

In Table 1 are given values of optical rotation for various solutions, containing 5 mgs to 38 mgs of Ag(I)/50 ml. Polarimetric determinations of Ag(I) have been compared with actual amount of Ag(I) taken in Table 2.

TABLE 1

*Optical rotation of solutions containing different amounts of silver in the form of an optically active complex*

Serial No.	Ag(I)/50 ml (mgs)	Optical rotation in degrees for Hg 5461
1	5.08	0.11
2	10.16	0.25
3	15.24	0.38
4	20.32	0.50
5	25.40	0.65
6	30.48	0.77
7	35.56	0.90
8	38.10	0.96

## DISCUSSION

A plot of concentration against optical rotation shows a linear relationship (Fig. 1).

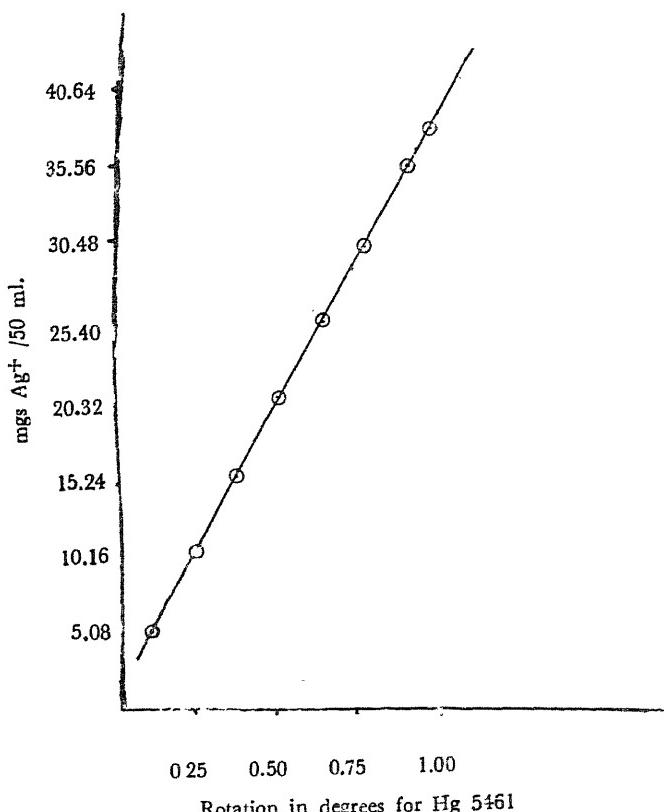


Fig. 1. Graph showing relationship between optical rotation and concentration.

The following equation for the curve was calculated by the method of least squares  $W = 0.678 + 38.7 R$  mgs of Ag(I)/50 ml where  $W$  is the weight of Ag(I)/50 ml in mgs and  $R$  is the angle of rotation in degrees. The degree of accuracy of this empirical equation has been shown in Table 2.

TABLE 2

Serial No.	Amount of Silver (mgs)		Difference (a) - (b) (mgs)
	Actual weight (a)	Polarimetrically estimated weight (b)	
1	5.08	4.94	+0.14
2	10.16	10.35	-0.19
3	15.24	15.38	-0.14
4	20.32	20.03	+0.29
5	25.40	25.83	-0.43
6	30.48	30.48	0.00
7	35.56	35.51	+0.05
8	38.10	37.83	+0.27

It is clear from Table 2 that polarimetric estimation of Ag(I) gives fairly accurate results in concentrations ranging from 5 mgs to 38 mgs of Ag (I) per 50 ml.

#### CONCLUSION

The polarimetric method can be employed to a fair degree of accuracy for determination of Ag(I) and it can be compared favourably with colorimetric methods<sup>8</sup>. The method can be made more useful by further increasing its sensitivity and accuracy in the following way :—

- (i) Recording of optical rotation in spectral region of the largest molecular rotation of active substance.
- (ii) Using an objective apparatus for noting rotation e.g., a photoelectric spectral polarimeter.

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# ON STEADY GAS FLOWS

By

G. PURUSHOTHAM and R. VENUGOPALA CHARI

*Department of Mathematics, Osmania University, Hyderabad-7, A. P.*

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## ABSTRACT

We consider the flow of a gas, which is inviscid, thermally nonconducting with the two specific heats constant, when the motion is steady. The intrinsic equations are expressed in terms of the flow quantities and properties of the flow are derived.

(a) If the streamlines are straight lines, density is uniform along the normal to the streamlines.

(b) Flow is sonic or isovels coincide with streamlines if the surfaces are minimal.

Variation of flow quantities, viz., entropy, enthaloy, and temperature along the tangent, (streamline) normal, and binormal are evaluated and the following properties are arrived at:

(1) curvature of the streamlines varies as the square of the Mach number along the binormal for a prim gas.

(2) Pressure is uniform if the streamlines are straight for a prim gas.

(3) If the flow is plane and homentropic and it is a Prim gas [8], it is irrotational.

(4) Coincidence of one of  $(T, P, q, p, p-h)$  = constant, with the streamlines implies the coincidence of the others also with the stream lines. This is more general than the result obtained by Prim [8], Kapur [2], and Purushotham and Chari [6].

(5) If entropy is constant on the binormal temperature is also constant.

(6) If entropy is constant on the normal and the streamlines are straight, temperature also remains constant on the normal.

(7) If the field is screw or Beltrami, then the normals to isotherms, isoentropics and Bernoulli surfaces are coincident.

(8) Normals to the surfaces  $(P, \rho, q, h, S, T, E)$  = constant are coplanar, a result more general than those obtained by Smith [8], Hansen and Martin [5], and Purushotham [7].

Suryanarayanan's [2] results are obtained in a more elegant manner.

## § 1. BASIC EQUATIONS

(A) The basic equations governing a steady gas (viz. an inviscid, thermally nonconducting, having two specific heats constant) in the absence of extraneous forces are given below in the conventional notation;

$$(1) \quad \overrightarrow{\operatorname{Div}} (\rho \vec{q}) = 0 \text{ (Continuity)}$$

$$(2) \quad \overrightarrow{\operatorname{Curl}} (\vec{q} \wedge \vec{q}) + \frac{1}{2} \nabla q^2 = (\vec{q} \cdot \nabla) \vec{q} = -\frac{1}{\rho} \nabla P \text{ (Momentum)}$$

$$(3) \quad \rho = \rho (P_1 S) \quad \text{(State)}$$

$$(4) \quad \vec{q} \cdot \nabla S = 0 \text{ (energy)}$$

$$(5) \quad q^2/2 + h (P_1 S) = \frac{a^2}{2} = h_o (p_o, S) \text{ (Enthalpy)}$$

$$\text{where } h (P_1 S) = \int_0^P \frac{dp}{\rho (P_1 S)}$$

$$(6) \quad \vec{q} \wedge \overrightarrow{\operatorname{Curl}} \vec{q} = \nabla \left\{ \frac{q^2}{2} + h (P_1 S) \right\} - T \nabla S \text{ (Crocco's Vorticity Equation)}$$

$$(7) \quad C^2 = \left( \frac{\partial P}{\partial \rho} \right) S \quad \text{(Speed of sound).}$$

## B. GEOMETRICAL RELATIONS

Considering  $t$ ,  $n$  and  $b$  as the unit tangents triply orthogonal vectors along the curves of congruences formed by the streamlines, their principal normals and binormal respectively and denoting  $ds$ ,  $dn$  and  $db$  as arc lengths along these curves and selecting  $\vec{r}$  as the position vector we have the following Frenet's formulae and other geometrical [11] relations :

$$(8) \quad \frac{\overrightarrow{d} \vec{v}}{ds} = \vec{t} = \vec{q}/q \quad (9) \quad \frac{d \vec{b}}{ds} = -\tau \vec{n} \quad (10) \quad \frac{d \vec{t}}{ds} = \vec{n} \vec{k}$$

$$(11) \quad \frac{\overrightarrow{d} \vec{n}}{ds} = \vec{b} \tau - \vec{t} \vec{k} \quad (12) \quad \frac{\overrightarrow{d} \vec{n}}{dn} = k' \vec{t} \quad (13) \quad \frac{\overrightarrow{d} \vec{b}}{db} = -\sigma' \vec{t}$$

$$(14) \quad \frac{\vec{dt}}{dn} = b \vec{\sigma}' - n \vec{k}' \quad (15) \quad \frac{d\vec{b}}{db} = k'' \vec{t} \quad (16) \quad \frac{\vec{d}n}{ds} = - \vec{\sigma}'' \vec{t}$$

$$(17) \quad \frac{d\vec{t}}{db} = \vec{n} \vec{\sigma}'' - \vec{b} \vec{k}'' \quad (17a) \quad \text{Div } \vec{t} = - (k' + k'') = J$$

where  $(k, k', k'')$ ,  $(\tau, \sigma', \sigma'')$ ,  $J$  and  $k$  are the curvatures, torsions and mean curvature of the above curves.

## § 2. INTRINSIC EQUATIONS

Using the above geometrical relations the basic equations of § 1 can be expressed as :

$$(18) \quad - (k' + k'') = J = - \left( \frac{d}{ds} \log p + \frac{d}{ds} \log q \right)$$

$$(19) \quad - \rho/2 \frac{dq^2}{ds} = \frac{dP}{ds}$$

$$(20) \quad - k \rho q^2 = \frac{dP}{dn}$$

$$(21) \quad \frac{dP}{d} = 0$$

$$(22) \quad \frac{ds'}{ds} = 0$$

$$(23) \quad - q \left( k q - \frac{dq}{dn} \right) = \frac{d}{dn} (h + q^2/2) - T \frac{ds}{dn}$$

$$(24) \quad q \cdot \frac{dq}{db} = \frac{d}{db} (h + q^2/2) - T \frac{ds}{da}$$

$$(25) \quad \text{Curl } \vec{q} = \vec{t} \cdot \vec{q} (\sigma' - \sigma'') + \vec{n} \frac{dq}{db} + \vec{b} \left( k q - \frac{dq}{dn} \right)$$

Using (3), (4), (7) and (19) in (18) we get

$$(26) \quad - J = (k' + k'') = \frac{d}{ds} \log q (M^2 - 1) = (-M^2) \frac{1}{f q^2} \frac{dP}{ds}$$

If the surfaces on which the curves for which  $n$  and  $b$  are unit tangents lie are minimal, then either isovels coincide with the stream lines or the flow is sonic everywhere.

Using (3) and (20) we get

$$(26a) \quad \frac{d\rho}{dn} = - k \rho M^2 + \frac{\partial \rho}{\partial s} \cdot \frac{ds}{dn}$$

If the flow is homentropic or the fluid is barotropic or entropy vanishes along the principal normal (26a) reduces to

$$(26b) \quad KM^2 = - \frac{d}{dn} \log \rho$$

which shows that the density of the fluid decreases along the normal to the streamlines. If the streamlines are straight the density is uniform along the normal to the streamline.

### § 3. VARIATION OF FLOW QUANTITIES (ENTROPY, ENTHALPY AND TEMPERATURE)

In this section we shall obtain the variation of the above quantities along the streamline, its principal normal and binormal.

#### A. VARIATION OF ENTROPY

Operating grad on (4) we get

$$(27) \quad \nabla \rho = \frac{\partial \rho}{\partial P} \nabla P + \frac{\partial \rho}{\partial S} \nabla S = \frac{1}{c^2} \nabla P + \frac{\partial \rho}{\partial S} \nabla S$$

Taking scalar product with  $\overset{\rightarrow}{n}$ ,  $\overset{\rightarrow}{b}$  and using (20) and (21) we get

$$(28a) \quad \frac{dP}{dn} = \frac{1}{\frac{\partial \rho}{\partial P}} \left( \frac{d\rho}{dn} + k \rho M^2 \right) \quad (28b) \quad \frac{dS}{ds} = 0$$

$$(29) \quad \frac{dS}{db} = \frac{1}{\frac{\partial \rho}{\partial S}} \cdot \frac{d\rho}{ab}$$

These determine the variations of entropy along the streamline, principal normal and binormal. For a Prim Gas [8] these become

$$(30) \quad \frac{dS}{dn} = - \gamma \text{Jev} \left[ k M^2 + \frac{d}{dn} \log \rho \right] \quad (31) \quad \frac{dS}{db} = - \gamma \text{Jev} \frac{d}{dn} \log \rho$$

Eliminating  $\rho$  and  $S$  from (30) and (31) by means of cross differentiation we obtain

$$(32) \quad \frac{d}{db} (k M^2) = 0$$

This shows that curvature of the streamline varies as the square of the Mach number along the binormal.

If in addition, the streamlines are straight (30) and (31) give

$$(33) \quad \overset{\rightarrow}{q} \cdot \nabla s = - \gamma \text{Jev} \overset{\rightarrow}{q} \cdot \nabla \log \rho = 0$$

which shows iso-pycnics are also straight. From (2), (3) and (20) we see that the pressure is uniform in this case.

For a plane Prim rotational isentropic flow, the expression for vorticity obtained by Thomas [10] and Prem Kumar [4] as

$$(34) \quad \zeta = \frac{P}{\rho g R} \cdot \frac{dS}{dn} \text{ where } R = J \text{ ev} (\gamma - 1)$$

From (34), we conclude that for a plane Prim gas, homentropy implies the irrotationality and the converse.

#### B. VARIATION OF ENTHALPY

Using (2) and (6), we obtain

$$(35) \quad \frac{1}{\rho} \nabla \rho = \nabla h - T \cdot \nabla S$$

Taking scalar product of (35) by  $\vec{i}$  and using (19), we get

$$(36) \quad \frac{1}{\rho} \frac{d\rho}{dS} = - \frac{dh}{dS} = q \frac{dq}{dS} = c^2/\rho \frac{dp}{dS}$$

From this we conclude that coincidence of any of  $(P, \rho, q, h) = \text{constant}$  with the streamlines implies the coincidence of remaining three with the streamlines. This is more general than proved in [2, 5, 6].

Taking scalar product of (35) by  $\vec{n}$  and using (4), (20) and (27), we get

$$(37) \quad \frac{dh}{dn} = - kq^2 + T / \frac{d\rho}{dS} \left( k \rho M^2 + \frac{dp}{dn} \right)$$

This gives the variation of enthalpy along the principal normal. For Prim gas, this becomes

$$(38) \quad \frac{dh}{dn} = - \left[ k M^2 (c^2 + T \times \text{Jev}) + T \times \text{Jev} \frac{d}{dn} \log \rho \right].$$

Taking the scalar product of (35) by  $\vec{b}$  and using (21) and (29), we get

$$(39) \quad \frac{\partial \rho}{\partial s} \cdot \frac{dh}{db} = T \cdot \frac{dp}{db}$$

From this we conclude that if the normal to the iso-pycnics lies in the osculating plane either the flow is homentropic or enthalpy is constant along binormal. For a Prim gas, this simplifies to

$$(40) \quad \frac{dh}{d} = - \times \text{Jev} T \frac{d}{db} \log \rho .$$

### C. VARIATION OF TEMPERATURE

Operating curl on (35), we get

$$(41) \quad \frac{1}{\rho^2} \nabla \rho \wedge \nabla P = \nabla T \wedge \nabla S$$

Using (3) and (41), we have

$$(42) \quad \frac{1}{\rho^2} \frac{\partial \rho}{\partial S} \nabla S \wedge \nabla P = \nabla T \wedge \nabla S \quad \text{which yields}$$

$$(43) \quad - \frac{1}{\rho^2} \frac{\partial \rho}{\partial S} \frac{dS}{db} \cdot \frac{dP}{dn} = \frac{dT}{dn} \cdot \frac{dS}{db} - \frac{dT}{db} \frac{dS}{dn}$$

$$(44) \quad \frac{dS}{db} \left( \frac{1}{\rho^2} \frac{\partial \rho}{\partial S} \frac{dP}{dS} + \frac{dT}{dS} \right) = 0 \text{ and}$$

$$(45) \quad \frac{dS}{dn} \left( \frac{1}{\rho^2} \frac{\partial \rho}{\partial S} \frac{dP}{dS} + \frac{dT}{dS} \right) = 0$$

when the flow is isentropic, we have

$$(46) \quad \frac{dT}{dS} = - \frac{1}{\rho^2} \frac{\partial \rho}{\partial S} \frac{dP}{dS} = \frac{dP}{dS} \frac{\partial}{\partial S} \left( \frac{1}{\rho} \right)$$

Using (46) and (36), we have

$$(47) \quad \frac{dT}{dS} \cdot \frac{1}{\frac{\partial}{\partial S}} \left( \frac{1}{\rho} \right) = \frac{dp}{dS} = \rho \frac{dh}{dS} = - \rho q \frac{dq}{dS} = c^2 \frac{dp}{dS}.$$

From this we find that coincidence of any one of  $(T, P, q, h, \rho) = \text{constant}$  with the streamlines implies the coincidence of the others. This is more general than the result proved by Prim [5], Kapur [2], and Purushotham and Chari [6]. From (43) it follows that

(a) when the entropy is constant along the binormal, temperature is also constant along it.

(b) when entropy is constant along the normal and the streamlines are straight, temperature is also constant on the normal.

#### D. BERNOULLI SURFACES

The equation (6) can be written as

$$(48) \quad \nabla \cdot \vec{B} = T \cdot \vec{\nabla} S + \vec{q} \wedge \text{curl } \vec{q}$$

where  $B = h + \frac{q^2}{2}$  = constant is defined to be the Bernoulli Surfaces [9]

Taking scalar product of (48) by  $\vec{t}$  and using (4), we get

$$(49) \quad \vec{t} \cdot \nabla \cdot \vec{B} = 0, \quad \text{which shows that the Bernoulli surfaces contain streamlines.}$$

If the flow is homentropic, taking scalar product of (43) we get

$$(50) \quad \text{Curl } \vec{q} \cdot \nabla \cdot \vec{B} = 0$$

This shows that in this case, Bernoulli surfaces also contain the vortex lines. These two results are derived by Masotti [3] and Suryanarayanan [9].

When the velocity field is scr w or Beltrami, i.e.  $\vec{q} \wedge \text{curl } \vec{q} = 0$  operating curl on (48), we get

$$(51) \quad \nabla \cdot \vec{T} \wedge \nabla \cdot \vec{S} = 0 \quad \text{and} \quad (52) \quad \nabla \cdot \vec{B} \wedge \nabla \cdot \vec{T} = 0$$

These show that the normals to the iso-therms, isentropics and Bernoulli surfaces are coincident for a Beltrami field

Using (4), (8) and (25), in (48), we get

$$(53) \quad \frac{dB}{dn} = T \frac{dS}{dn} - q \left( kq - \frac{dq}{dn} \right) = \frac{T}{\frac{\partial p}{\partial S}} \left( kPM^2 + \frac{dp}{dn} \right) - q \text{curl } \vec{q} \cdot \vec{b}.$$

$$(54) \quad \frac{dB}{dt} = \frac{T}{\frac{\partial p}{\partial S}} \frac{dp}{dt} + q \frac{di}{dh} = \frac{T}{\frac{\partial p}{\partial S}} \frac{dp}{dt} + q \text{curl } \vec{q} \cdot \vec{n}$$

These give the variation of  $h + \frac{q^2}{2} = B$  along principal normal and binormal to the streamline. From these it is clear that normal to the Bernoulli surface lies in the normal plane.

For a Prim gas, (53) and (54) become

$$(55) \quad \frac{dB}{dn} = -T \times \text{Jev} \left( kM^2 + \frac{d}{dt} \log p \right) - \text{curl } \vec{q} \cdot \vec{b}$$

$$(56) \quad \frac{dB}{db} = - T \propto \text{Jev} \quad \frac{d}{db} \log \rho + q \text{curl } \overset{\rightarrow}{q} \cdot \overset{\rightarrow}{n}$$

Taking scalar product of (48) by  $\nabla P$  and using (20), we get

$$(57) \quad \nabla \rho \cdot \nabla B = - \rho k q^2 \left[ T \frac{dS}{dn} - q \left( kq - \frac{dq}{dn} \right) \right]$$

From this it follows that the normals to the isobars and Bernoulli surfaces are orthogonal if any one of the following conditions is satisfied :

(i) streamlines are straight

(ii) The flow is homentropic and the vorticity lies in the osculating plane.

The converse of the above is also true. (A result proved by Suryanarayanan [9]).

But in condition (ii), imposition of homentropy for spatial flows is unnecessary,

Since  $\frac{dS}{db}$  need not be zero, even if  $\frac{dS}{dn} = 0$

### § 4. (A) COMPLEX LAMELLAR FLOWS

A complex lamellar flow is one in which the streamlines are normal to a one parameter family of surfaces, i. e. it is a field of the type

$$(58) \quad \overset{\rightarrow}{q} = \alpha \text{grad } \phi .$$

where  $\alpha$  and  $\phi$  are scalar point functions. The surface defined by  $\phi = \text{constant}$  is defined to be the Beltrami surface [9]. From (58) it is evident that the normal to the Beltrami surface is perpendicular to the normal plane. For this field, the condition for the streamlines to be intersected normally by a one parameter family of surfaces is

$$(59) \quad \overset{\rightarrow}{q} \cdot \text{Curl } \overset{\rightarrow}{q} = 0$$

Now substituting for  $\overset{\rightarrow}{q}$  and  $\text{Curl } \overset{\rightarrow}{q}$  from (8) and (25), we get

$$(60) \quad \sigma' - \sigma'' = 0 \text{ Using this in (25) we get}$$

$$(61) \quad \text{Curl } \vec{q} = \vec{n} \frac{dq}{d\theta} + \vec{n} \left( hq - \frac{\partial q}{\partial n} \right)$$

which shows that for a complex lamellar flow the vorticity lies in the normal plane. This has been proved by Purushotham and Chari [6] and Suryanarayanan [9].

Using (58) in (59), we get

$$(62) \quad \vec{\nabla} \phi \cdot \text{Curl } \vec{q} = 0$$

which shows that the Beltrami surface contains vortex lines. In a previous section, we also proved for homentropic flow that the Bernoulli surfaces also contain vortex lines. Hence, we conclude that for homentropic complex lamellar flow, Bernoulli and Beltrami surfaces intersect orthogonally along the vortex lines. This has been shown by Suryanarayanan [9] by a circuitous method.

(B) We shall now prove that normals to the Bernoulli surfaces, iso-bars, iso-phonics, iso-vels, iso-therms isentropics and equi-enthalpy lines are coplanar.

Taking the vector product of (41) by  $\vec{\nabla} T \wedge \vec{\nabla} S$ , we get

$$(63) \quad (\vec{\nabla} P \wedge \vec{\nabla} T) \wedge (\vec{\nabla} T \cdot T \wedge \vec{\nabla} S) = 0$$

Taking the vector product of (48) by  $\vec{\nabla} T$ , we have

$$(64) \quad \vec{\nabla} T \wedge \vec{\nabla} B = \vec{\nabla} T \wedge (q \wedge s) + T (\vec{\nabla} T \wedge \vec{\nabla} s)$$

Now taking the vector product of (64) by  $\vec{\nabla} P \wedge \vec{\nabla} T$  and using (63) together with the result proved by Purushotham [7], we obtain

$$(65) \quad (\vec{\nabla} T \wedge \vec{\Delta} B) \wedge (\vec{\nabla} P \wedge \vec{\nabla} T) = 0$$

Eliminating pressure, by operating curl on (35), we get

$$(66) \quad (\vec{\nabla} P \wedge \vec{\nabla} h) = P \vec{\nabla} T \wedge \vec{\nabla} S + T \vec{\nabla} P \wedge \vec{\nabla} S$$

Taking vector product of (66) by  $(\vec{\nabla} T \wedge \vec{\nabla} P)$  and using (63), we get

$$(67) \quad (\vec{\nabla} P \wedge \vec{\Delta} h) \wedge (\vec{\nabla} T \wedge \vec{\nabla} P) = 0$$

From (63), (65), (67), together with the result proved in [7] we conclude that the normals to the surfaces  $(P, \rho, q, h, B, S, T) = \text{constant}$  are coplanar.

This is more general than the one proved by Smith [8], Purushotham [7] and Hansen and Martin [1].

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## POLARIMETRIC ESTIMATION OF COBALT

By

O. N. PERTI and I. PRAKASH

*Chemical Laboratories, Th. D. S. B. Govt. College, Naini Tal, U. P.*

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### ABSTRACT

A fairly accurate and rapid method for estimation of cobalt is possible polarimetrically. Cobalt (II) is converted into potassium cobalticyanide with the help of potassium cyanide and hydrogen peroxide. Yellow coloured solution of potassium cobalticyanide is rendered acidic by adding a few drops of acetic acid solution and then cobalt is precipitated by using strychnine acetate solution as precipitant. The precipitate of optically active compound is filtered, washed, dissolved in acetone-water mixture and determined polarimetrically using following empirical equation.

$$W = 12.3 R - 0.1936 \text{ mgs of Co(II)/50 ml}$$

where  $W$  = mgs of Co(II)/50 ml and  $R$  is the angle of rotation in degrees.

### INTRODUCTION

Alkaloids have been used as sensitive analytical reagents for detection as well as determination of metals. Liteanu and Cosma<sup>1</sup> have made use of such reactions in carrying out the estimation of Hg(II) by measuring the optical rotation of complex formed by quinine with potassium-iodomercurate. Knowing the angle of rotation for a solution of complex in acetone, the weight of Hg(II) in given volume of solution was calculated with the help of an empirical equation, deduced on the basis of experimental data. This method has been extended by us in polarimetric estimations of cadmium<sup>2</sup> and bismuth<sup>3</sup>. The present paper gives a method for polarimetric estimation of Co(II) based on similar principle.

Number of reactions are known in literature where alkaloids have been used as microchemical reagents for detection of cyano complexes of metals. For example, formation of crystalline precipitate by cocaine with ferrocyanide and ferricyanide can be used for the microchemical detection of these substances<sup>4</sup>. Martini<sup>5</sup> has reported that concentrated solution of quinidine sulphate in acetic acid is suitable for the microchemical detection of  $0.1\gamma$  of the ferricyanide ion. Wagenaar<sup>6</sup> has discovered the interference of ferricyanide and ferrocyanide ions during sensitive test for chromate with brucine. This led us to study the reaction of cobalticyanide (III) with strychnine and we found the reaction to be fairly sensitive for purposes of polarimetric estimation of Co(II).

## EXPERIMENTAL

Solution of cobalt nitrate of concentration 1.01 mgs of Co(II)/ml was used.

To an aliquot of cobalt nitrate solution, potassium cyanide solution was added in excess till a persistent brown colour was obtained. To the resulting solution was then added a few drops of hydrogen peroxide and the whole was boiled. In order to avoid the precipitation of alkaloid, the final solution was rendered acidic by adding a few drops of dilute acetic acid solution. The precipitation of optically active compound was done by addition of 2.5% solution of strychnine acetate in slight excess. It was noted that for complete precipitation of 1 mg of Co(II), 50 mgs of strychnine was more than sufficient. To ensure complete precipitation, beaker containing the precipitate was left undisturbed for sometime at room temperature and then finally cooled in ice. The precipitate was filtered, washed with a few ml of petroleum ether and dissolved in 50 ml of acetone-water (3:7) mixture. This solution was used for polarimetric measurement at room temperature (21°C.), using a two decimeter tube.

In Table 1, values of optical rotations for various solutions, containing 1 mg to 10 mgs of Co(II)/50 ml are recorded.

In Table 2, polarimetric estimations for Co(II) have been compared with gravimetric determination of cobalt as anthranilate<sup>7</sup>.

TABLE I

Optical rotations of solutions containing different amount of cobalt  
in the form of optically active compound

Serial no.	Co(II)/50 ml (mgs)	Optical rotation in degrees for Hg 5461
1	1.01	0.09
2	2.02	0.18
3	4.04	0.35
4	6.06	0.52
5	8.08	0.67
6	10.10	0.83

## DISCUSSION

A plot of concentration against optical rotation shows a linear relationship (Fig. 1).

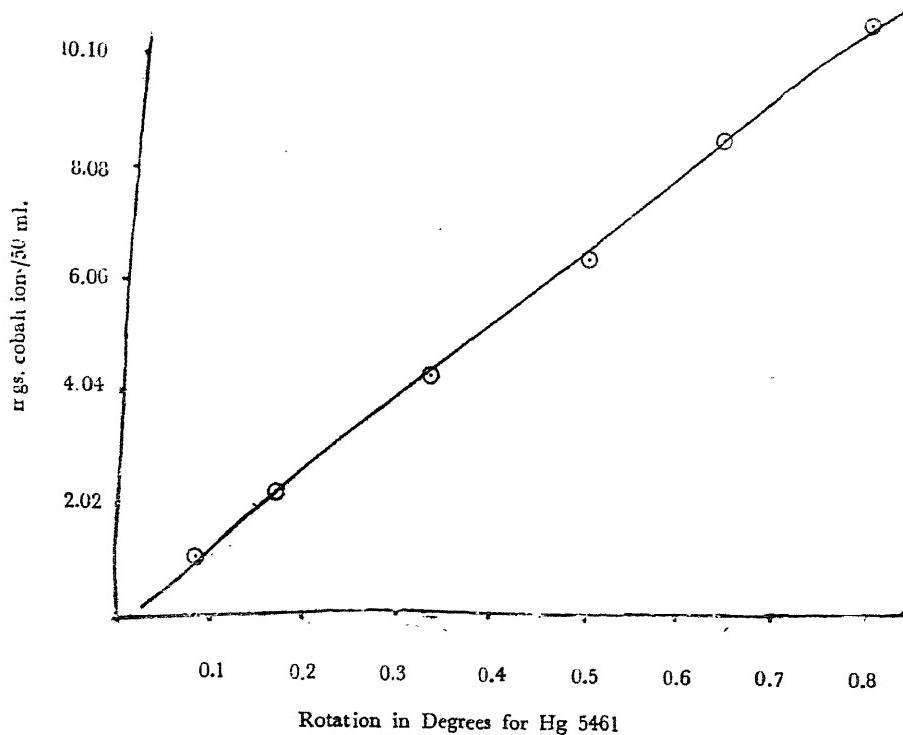


Fig. 1. Graph showing relationship between optical rotation and concentration.

On the basis of experimental data, the following equation of the curve was calculated by the method of least squares.

$$W = 12.3 R - 0.1936 \text{ mgs of Co(II)/50 ml}$$

where W is the weight of Co(II) per 50 ml in mgs and R is the angle of rotation in degrees. The degree of accuracy of this empirical equation has been shown in Table 2.

TABLE 2

Serial no.	Amount of Co(II) (mgs)		Difference (a)-(b) mgs
	Gravimetrically estimated (a)	Polarimetrically esti- mated (b)	
1	1.01	0.81	0.20
2	2.02	2.02	0.00
3	4.04	4.11	-0.07
4	6.06	6.20	-0.14
5	8.08	8.05	0.03
6	10.10	10.02	0.08

It is clear from Table 2 that polarimetric estimation of Co(II) gives fairly accurate results in concentrations ranging from 2 mgs to 10 mgs of Co(II) per 50 ml.

#### CONCLUSION

The polarimetric method of estimating cobalt, as described in this paper, is fairly accurate and it can well be compared with colorimetric methods of estimation<sup>8</sup>. This method has the advantage, over colorimetric method, of being quick and easy to perform. Its obvious advantage lies in routine and rapid estimation of metallic ions Co(II). Its accuracy and sensitivity can be further increased by noting optical rotation in the spectral region of largest molecular rotation of active substance (say ultraviolet) and by employing an objective apparatus, that is, photoelectrical method of recording rotations.

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ON GENERALIZED HANKEL AND MEIJER'S BESSEL  
FUNCTION TRANSFORMS

By

K. C. GUPTA

*Lecturer in Mathematics, M. R. Engineering College, Jaipur*

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ABSTRACT

In this note first we prove a theorem relating a generalized Hankel transform of  $f(x)$  and Meijer's Bessel function transform of  $f'(x) g(x)$ . Later on we consider Meijer's Bessel function transform of a function which is selfreciprocal in the generalized Hankel transform. The theorems have been illustrated by certain suitable examples. A theorem recently obtained by Sharma (1963, p. 107) follows as particular case of our theorem.

1. The following notations will be used throughout this paper:—

$$L \left\{ f(x); p \right\} = \int_0^\infty e^{-px} f(x) dx \quad (1)$$

$$K_\mu \left\{ f(x); p \right\} = \int_0^\infty px^{\frac{1}{2}} K_\mu(px) f(x) dx \quad (2)$$

$$H_\nu \left\{ f(x); y \right\} = \int_0^\infty (xy)^{\frac{1}{2}} J_\nu(xy) f(x) dx \quad (3)$$

$$R_\nu \left\{ f(x); y, k, m \right\} = 2^{-\nu} \int_0^\infty (xy)^{\nu+\frac{1}{2}} X_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) f(x) dx \quad (4)$$

$$X_{\nu, k, m}(x) = x^{-\nu} G_{2, 4}^{2, 1} \left( x; \begin{matrix} k-m-\frac{1}{2}, \nu-k+m & \\ \nu, \nu+2m, -2m, 0 & \end{matrix} \right) \quad (5)$$

$$\Gamma(a \pm b) = \Gamma(a+b) \Gamma(a-b) \quad (6)$$

$${}_2F_1 \left( \begin{matrix} a \pm b \\ c \end{matrix}; x \right) = {}_2F_1(a+b, a-b; c; x) \quad (7)$$

(2) was introduced into mathematical analysis by Meijer [4] and will be called Meijer's Bessel function transform. It is a generalization of the well known Laplace transform. We have

$$K_{\pm\frac{1}{2}} \left\{ f(x); p \right\} = \left( \frac{\pi}{2} \right)^{\frac{1}{2}} L \left\{ f(x); p \right\} \quad (8)$$

Where  $L\{f(x); p\}$  denotes the Laplace transform of  $f(x)$ .

(4) was given first by Narain [5 p. 270]. It is a generalization of the Hankel transform which has been denoted symbolically by (3).

(4) reduces to (3) when  $k+m=\frac{1}{2}$ . It has also been established by Narain in the same paper that

$$\chi_{v, k, m}(x) \sim o(x^{m \pm m}) \text{ for small } x \quad (9)$$

and

$$\chi_{v, k, m}(x) \sim o(x^{-\eta}) \text{ for large } x \quad (10)$$

Where  $\eta$  stands for either of the three quantities

$$\frac{1}{2}(v+\frac{1}{2}), \frac{1}{2}+k-m, \frac{3}{2}+v+m-k.$$

Throughout this note  $\eta$  will stand for either of these three quantities.

*Theorem 1:* If  $y^{v+\frac{1}{2}-2\eta} R_v \left\{ f(x); y, k, m \right\} \in L(0, \infty)$ ,

$$x^{v+2m \pm \mu \pm 2m+1} g(x) \text{ and } x^{\frac{1}{2}} f(x) g(x) \in L(0, R),$$

$$R(\eta+m \pm m) > 0,$$

then

$$K_\mu \left\{ f(x) g(x); p \right\} = \int_0^\infty R_v \left\{ f(x); y, k, m \right\} R_v \left\{ (px)^{\frac{1}{2}} K_\mu (px) g(x); y, k, m \right\} dx \quad (11)$$

*Proof:* Since [5 p. 270],

$$f(x) = 2^{-v} \int_0^\infty (yx)^{v+\frac{1}{2}} \chi_{v, k, m} \left( \frac{x^2 y^2}{4} \right) R_v \left\{ f(x); y, k, m \right\} dy \quad (12)$$

we have

$$\begin{aligned} K_\mu \left\{ f(x) g(x); p \right\} &= 2^{-v} \int_0^\infty (px)^{\frac{1}{2}} K_\mu (px) g(x) \\ &\times \left[ \int_0^\infty (xy)^{v+\frac{1}{2}} \chi_{v, k, m} \left( \frac{x^2 y^2}{4} \right) R_v \left\{ f(x); y, k, m \right\} dy \right] dx \end{aligned} \quad (13)$$

On inverting the order of integration in (13) we get (11).

All that remains now is to justify the inversion of the order of integration.  
For this the integrals

$$\int_0^\infty |y^{\nu+\frac{1}{2}} \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) R_\nu \left\{ f(x); y, k, m \right\}| dy$$

and

$$\int_0^\infty |x^{\nu+1} K_\mu(p x) \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) g(x)| dx$$

should be convergent and one of the repeated integrals must exist.

By virtue of (9) and (10) we have :

$$y^{\nu+\frac{1}{2}} \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) R_\nu \left\{ f(x); y, k, m \right\}$$

$$\sim y^{\nu+\frac{1}{2}-2\eta} R_\nu \left\{ f(x); y, k, m \right\} \quad \text{for large } y$$

$$\sim y^{\nu+\frac{1}{2}+2m\pm 2m} R_\nu \left\{ f(x); y, k, m \right\} \quad \text{for small } y$$

Thus  $y$ -integral is absolutely convergent when

$$y^{\nu+\frac{1}{2}-2\eta} R_\nu \left\{ f(x); y, k, m \right\} \in L(0, \infty) \text{ and } R(\eta+m\pm m) > 0$$

$$\text{Again } x^{\nu+1} K_\mu(p x) \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) g(x)$$

$$\sim x^{\nu+\frac{1}{2}-2\eta} e^{-px} g(x) \quad \text{for large } x,$$

$$\sim x^{\nu+1\pm\mu+2m\pm 2m} g(x) \quad \text{for small } x.$$

So  $x$ -integral is convergent when

$$x^{\nu+1\pm\mu+2m\pm 2m} g(x) \in L(0, R).$$

Also the repeated integral exists if  $f(x) g(x) x^{\frac{1}{2}} \in L(0, R)$ . Therefore inversion of the order of integration is justified under the conditions stated with the theorem by virtue of De La Vallee' Poussin's theorem [1, p. 504].

*Corollary 1:* On putting  $k + m = \frac{1}{2}$  in (11), the theorem reduces to a known result due to Sharma [6, p. 108].

*Corollary 2:* When we take  $g(x) = x^\lambda$  in the theorem we get

$$\begin{aligned} K_\mu \left\{ x^\lambda f(x); p \right\} &= 2^\lambda p^{\nu - \lambda - 3/2} \int_0^\infty y^{\frac{1}{2} - \nu} R_\nu \left\{ f(x); y, k, m \right\} \\ &\times G_{4,4}^{2,3} \left( \frac{y^2}{p^2} \middle| \frac{\nu - \lambda - \mu}{2}, \frac{\nu - \lambda + \mu}{2}, k - \frac{1}{2} - m, m + \nu - k + \frac{1}{2} \right) dy \quad (14) \end{aligned}$$

$\nu, \nu + 2m, -2m, 0$

Where  $y^{\nu + \frac{1}{2} - 2m} R_\nu \left\{ f(x); y, k, m \right\} \in L(0, \infty)$ ,  $x^{\lambda + \frac{1}{2}} f(x) \in L(0, R)$ ,

$R(\nu + \lambda + 2m \pm 2m \pm \mu + 2) > 0$  and  $R(\eta + m \pm m) > 0$ .

*Example 1.* If we take

$$f(x) = x^{\nu + 2m + \frac{1}{2}} K_{2m}(ax)$$

then we have [3, p. 187]

$$\begin{aligned} K_\mu \left\{ x^\lambda f(x); p \right\} &= 2^{\nu + 2m + \lambda - 1} a^{2m} p^{-\nu - 4m - \lambda - 3/2} \\ &\times \frac{\Gamma_2(\nu + 2m + \lambda \pm \mu \pm 2m + 2)}{\Gamma(\nu + 2m + \lambda + 2)} {}_2F_1 \left( \begin{matrix} \frac{1}{2}(\nu + 2m + \lambda \pm \mu \pm 2m + 2) \\ \lambda + 2m + \nu + 2 \end{matrix}; 1 - \frac{a^2}{p^2} \right) \end{aligned}$$

Where  $R(a+p) > 0$  and  $R(\nu + 2m + \lambda \pm \mu \pm 2m + 2) > 0$ .

Also [5, p. 281] gives

$$\begin{aligned} R_\nu \left\{ f(x); y, k, m \right\} &= \frac{2^{\nu + 2m} a^{1-2k} \Gamma(\nu + 2m - k \pm m + 3/2)}{\Gamma(\nu + 2m - 2k + 2)} \\ &\times y^{2k - 2m - \nu - 5/2} {}_2F_1 \left( \begin{matrix} \nu + 2m - k \pm m + 3/2 \\ \nu + 2m - 2k + 2 \end{matrix}; -\frac{a^2}{y^2} \right) \end{aligned}$$

provided that  $R(\nu + 2m \pm 2m + 1) > 0$  and  $R(a) > 0$ .

Applying (14) to the values of  $K_\mu \left\{ x^\lambda f(x); p \right\}$  and

$R_\nu \left\{ f(x); y, k, m \right\}$  thus obtained we get

$$\begin{aligned}
& \int_0^\infty y^{2k-2m-2v-2} {}_2F_1 \left( \begin{matrix} v+3/2-k+2m \pm m \\ v+2m-2k+2 \end{matrix}; -\frac{a^2}{y^2} \right) \\
& \times G_{4,4}^{2,3} \left( \begin{matrix} \frac{y^2}{p^2} \\ \frac{v-\lambda+\mu}{2}, \frac{v-\lambda-\mu}{2}, k-m-\frac{1}{2}, m+v-k+\frac{1}{2} \end{matrix}; \begin{matrix} v, v+2m, -2m, 0 \end{matrix} \right) dy \\
= & \frac{2m+2k-1}{2p^{2v+4m}} \frac{\Gamma(\frac{1}{2}(v+2m+\lambda \pm \mu \pm 2m+2)) \Gamma(v+2m-2k+2)}{\Gamma(v+2m \pm m-k+3/2) \Gamma(v+2m+\lambda+2)} \\
& \times {}_3F_2 \left( \begin{matrix} \frac{1}{2}(v+2m+\lambda \pm \mu \pm 2m+2) \\ v+2m+\lambda+2 \end{matrix}; 1-\frac{a^2}{p^2} \right)
\end{aligned} \tag{15}$$

Where  $R(v+2m+\lambda-2k \pm \mu+3) > 0$ ,  $R(v+2m-2k+2) > 0$ ,

$R(v+1) > 0$  and  $R(v+1+4m) > 0$ .

(15) reduces to a result obtained by Sharma [6, p. 109] if we take  $k+m=\frac{1}{2}$  in it.

3. The following result can be obtained with the help of [2, p. 422] and will be required later on:

$$\begin{aligned}
& R_v \left\{ x^{2\rho-\frac{1}{2}} G_{\gamma, \delta}^{\alpha, \beta} \left( \lambda x^2 \left| \begin{matrix} a_1, \dots, a_\gamma \\ b_1, \dots, b_\delta \end{matrix} \right. \right); y, k, m \right\} \\
= & \left( \frac{2}{y} \right)^{2\rho} y^{-\frac{1}{2}} G_{\gamma+4, \delta+2}^{\alpha+1, \beta+2} \left( \frac{4\lambda}{y^2} \left| \begin{matrix} a_1, \dots, a_\beta \\ b_1, \dots, b_\alpha \end{matrix} \right. \right. \\
& \left. \left. \begin{matrix} \frac{1}{2}-\rho-v/2, \frac{1}{2}-\rho-v/2-2m, v/2-\rho+\frac{1}{2}+2m, v/2-\rho+\frac{1}{2}, a_\beta+1, \dots, a_\gamma \\ v/2+m+1-\rho-k, k-m-v/2-\rho, b_{\alpha+1}, \dots, b_\delta \end{matrix} \right. \right)
\end{aligned} \tag{16}$$

Where  $R(v+2\rho+2m \pm 2m+2b_j+1) > 0$ ,  $\alpha+\beta > \frac{1}{2}(\gamma+\delta)$

$|\arg \lambda| < (\alpha + \beta - \frac{1}{2}\gamma - \frac{1}{2}\delta)\pi$  and  $R(2\eta-v-2\rho+1-2a_h) > 0$ .

$(j = 1, 2, \dots, \alpha; h = 1, 2, \dots, \beta)$

(16) reduces to a known result [2, p. 91] when  $k+m=\frac{1}{2}$ .

*Example 2.* On taking  $g(x) = x^{s-\lambda-3/2} J_\rho(ax)$  and  $f(x) = x^\lambda K_\sigma(bx)$  we have with the help of (16).

$$R_v \left\{ f(x); y, k, m \right\} = 2^{\lambda-\frac{1}{2}} b^{-\lambda} y^{-1}$$

$$\times G_{4,4}^{2,3} \left( \frac{y^2}{b^2} \left| \begin{matrix} 1 - \frac{1}{2}\lambda - \frac{1}{2}\sigma, 1 - \frac{1}{2}\lambda + \frac{1}{2}\sigma, \frac{1}{4} + k - \nu/2 - m, 5/4 + \nu/2 + m - k \\ \frac{3}{4} + \nu/2, \frac{3}{4} + \nu/2 + 2m, \frac{3}{4} - \nu/2 - 2m, \frac{3}{4} - \nu/2 \end{matrix} \right. \right)$$

Where  $R(b) > 0$  and  $R(\lambda + \nu + 2m \pm \sigma \pm 2m + 3/2) > 0$

$$R \left\{ (px)^{\frac{1}{2}} K_\mu (px) g(x); y, k, m \right\} = p^{\frac{1}{2}} 2^{-\nu}$$

$$\times \int_0^\infty (xy)^{\nu + \frac{1}{2}} \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) x^{s - \lambda - 1} J_\rho (ax) K_\mu (px) dx$$

Where  $R(\nu + 2m \pm 2m + s + \rho - \lambda \pm \mu + \frac{1}{2}) > 0$  and  $R(p) > 0$ .

Also by virtue of (2) we have

$$K_\mu \left\{ f(x) g(x); p \right\} = p^{\frac{1}{2}} \int_0^\infty x^{s-1} J_\rho (ax) K_\sigma (bx) K_\mu (px) dx \quad (17)$$

provided that this integral exists.

Evaluating (17) with the help of Sharma [6, p. 110] and applying (11) we get that if  $\theta(y) \in L(0, \infty)$ ,  $R(2\nu + 1) > 0$ ,

$$R(2\nu + 4m + 1) > 0, R(m - k + 1) > 0 \text{ and } R(\lambda - \nu \pm \sigma + \frac{1}{2}) > 0$$

then

$$\int_0^\infty y^{\nu - \frac{1}{2}} G_{4,4}^{2,3} \left( \frac{y^2}{b^2} \left| \begin{matrix} 1 - \frac{1}{2}\lambda - \frac{1}{2}\sigma, 1 - \frac{1}{2}\lambda + \frac{1}{2}\sigma, k + \frac{1}{4} - \nu/2 - m, 5/4 + \nu/2 + m - k \\ \frac{3}{4} + \nu/2, \frac{3}{4} + \nu/2 + 2m, \frac{3}{4} - \nu/2 - 2m, \frac{3}{4} - \nu/2 \end{matrix} \right. \right) \theta(y) dy$$

$$= b^\lambda 2^{s + \nu - \lambda - 5/2} \sum_{\sigma, -\sigma} \frac{a^\rho b^\sigma \Gamma(-\sigma) \Gamma \frac{1}{2}(s + \sigma \pm \mu - \rho)}{\Gamma(1 + \rho) p^{s + \rho + \sigma}}$$

$$\times F_4 \left( \frac{s + \sigma + \rho - \mu}{2}, \frac{s + \sigma + \rho + \mu}{2}; 1 + \rho, 1 + \sigma; -\frac{a^2}{p^2}, \frac{b^2}{p^2} \right). \quad (18)$$

$$\text{Where } \theta(y) = \int_0^\infty x^{\nu + s - \lambda - \frac{1}{2}} J_\rho(ax) K_\mu(px) \chi_{\nu, k, m} \left( \frac{x^2 y^2}{4} \right) dx$$

On putting  $k + m = \frac{1}{2}$  in (18) we get after slight changes in the parameters

$$\int_0^\infty y^{\gamma - 1} {}_2F_1(\alpha, \beta; \gamma; -by) F_4(\xi, \sigma; \zeta, \gamma; -ax, -cy) dy$$

$$= \sum_{\alpha, \beta} \frac{c^{\alpha-\gamma} \{ \Gamma(\gamma) \}^2 \Gamma(\beta-\alpha)}{b^\alpha \Gamma(\alpha) \Gamma(\beta)} \frac{\Gamma(\alpha+\xi-\gamma)}{\Gamma(\xi)} \frac{\Gamma(\alpha+\sigma-\gamma)}{\Gamma(\sigma)} \\ \times F_4 \left( \alpha+\xi-\gamma, \alpha+\sigma-\gamma; \zeta, \alpha-\beta+1; -ac, \frac{c}{b} \right) \quad (19)$$

for  $R(\alpha+\xi-\gamma) > 0$ ,  $R(\alpha+\sigma-\gamma) > 0$ ,  $R(\beta+\xi-\gamma) > 0$ ,

$$R(\beta+\sigma-\gamma) > 0, a, b, c > 0.$$

(19) was given by Sharma [6, p. III]. There was a slight misprint in his result. Second variable of  $F_4$  should have been  $\frac{c}{b}$  and not  $-\frac{c}{b}$ .

4.  $f(x)$  is said to be selfreciprocal in the generalized Hankel transform if it satisfies the relation

$$f(x) = 2^{-v} \int_0^\infty (xy)^{v+\frac{1}{2}} \chi_{v, k, m} \left( \frac{x^2 y^2}{4} \right) f(y) dy \quad (20)$$

*Theorem 2.* If  $f(x)$  is selfreciprocal in the generalized Hankel transform,

$$y^{v+\frac{1}{2}-2\eta} f(x) \in L(0, \infty), R(\eta+m \pm m) > 0,$$

$x^{v+1 \pm \mu + 2m \pm 2m} g(x) \in L(0, R)$ , and  $x^{\frac{1}{2}} f(x) g(x) \in L(0, R)$ , then by virtue of the theorem 1 we have

$$K_\mu \left\{ f(x); p \right\} = \int_0^\infty R_v \left\{ (px)^{\frac{1}{2}} K_\mu(px) g(x); y, k, m \right\} f(y) dy \quad (21)$$

*Corollary.* Since [5, p. 286] a function which is selfreciprocal in the transform defined by (4) becomes selfreciprocal in Hankel transform when  $k+m=\frac{1}{2}$ , on putting  $k+m=\frac{1}{2}$  in (21) we see that if  $f(x)$  is selfreciprocal in the Hankel transform, then

$$K_\mu \left\{ f(x); p \right\} = \frac{\Gamma \frac{1}{2} (v \pm \mu + 2)}{p^{v+3/2} \Gamma(v+1)} \int_0^\infty y^{v+\frac{1}{2}} \\ \times {}_2F_1 \left( \frac{v \pm \mu + 2}{2}; \frac{-y^2}{p^2} \right) f(y) dy \quad (22)$$

Where  $f(x) \in L(0, \infty)$ ,  $R(3/2 \pm \mu) > 0$  and  $R(v + \frac{1}{2}) > 0$ .

*Example 3.* If we take the following selfreciprocal function in the Hankel transform

$$x^{v+2m+\frac{1}{2}} {}_2F_1 \left( 2m+v+1; v+m+1; -\frac{x^2}{2} \right)$$

Where  $R(v+2m+1) > 0$

Then on evaluating  $K_\mu \left\{ f(x); p \right\}$  with the help of [3, p. 187] and applying (22) we obtain

$$\begin{aligned} & \int_0^\infty y^{2v+2m+1} {}_2F_1 \left( 2m+v+1; v+m+1; -\frac{y^2}{2} \right) \\ & \quad {}_2F_1 \left( \frac{v+2\pm\mu}{2}; v+1; -\frac{y^2}{p^2} \right) dy \\ & = \frac{2^v + 2^m}{p^{2m}} \frac{\Gamma(v+1)}{\Gamma(\frac{1}{2}(v+\mu+2))} \frac{\Gamma(v+m+1)}{\Gamma(2m+v+1)} \\ & \times E \left( \frac{v+2m+\mu+2}{2}, \frac{v+2m-\mu+2}{2}, v+2m+1 : v+m+1 : \frac{p^2}{2} \right) \quad (23) \end{aligned}$$

Where  $R(v+2m\pm\mu+2) > 0$ ,  $R(v+m+1) > 0$  and  $m > 0$ .

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